A Contribution to the Study of Oil-Field Water Analysis.*

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Part I.—Estimation of the Sulphate Radicle by Benzidine and Errors Inherent in the Method.

The series of experiments recounted in this paper were made with the following objects in view :—

1. To standardise a method of sulphate estimation suitable for the routine analysis of oil-field waters.
2. To determine the errors inherent in such a method and to estimate their numerical dimensions under specific conditions, thus obtaining a suitable set of graphs.
3. To ascertain the reason for the observed discrepancies.

Historical Development.

The first mention of the use of insoluble benzidine and tolidine sulphates in analysis was made by Vaubel[1]; he employed this characteristic in connection with the estimation of the purity of commercial benzidine and tolidine. The two bases were precipitated from hydrochloric acid solution by the addition of an excess of sulphuric acid or of sulphate, a correction being applied for the solubility of the respective sulphates. This correction is of great importance and shows increasing solubility with increasing hydrochloric acid concentration :—

	Benzidine.	Tolidine (as sulphates).
1 litre of water dissolves	0.0076	0.03g.
1 litre of water + 20 ml. 35% HCl dissolves	0.02	0.513g.
1 litre of water + 50 ml. 35% HCl dissolves	0.48	4.42g.

(For solubility of benzidine sulphate see also Bisson and Christie.[2])

Vaubel's investigations were extended and developed by Müller,[3] who actually standardized the method for the estimation of sulphates or sulphuric acid, using a solution of benzidine hydrochloride.

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[1] *Zeits. Anal. Chem.*, 1896, **35**, 163.
[2] *Ind. Eng. Chem.*, 1920, **12**, 485.
[3] *Ber.*, 1902, **35**, 1587; *Z. Angew Chem.*, 1903, **16**, 1017.

The method adopted is of interest; the acidity of a solution of benzidine hydrochloride is determined before and after the addition of a neutral sulphate, the insoluble benzidine sulphate having been removed by filtration. Müller employed the method which is common practice at the present time of using baryta or alkali hydroxide and phenol phthalein.

The following year a modification of Müller's method was proposed by Raschig,[4] who worked with the precipitated benzidine sulphate. He showed that benzidine sulphate is hydrolysed quantitatively when heated with a large excess of water, a property which is in accordance with the nature of a weak base. Thus Raschig extended the research and made it possible to work with acid solutions of sulphates or with sulphuric acid. As a result of adverse criticism of this method by Müller,[5] who based his contentions on the error introduced on account of the solubility of benzidine sulphate, Raschig[6] suggested a modified solution[7] of benzidine hydrochloride and the reduction of the volume of wash water to 5 ml.

Müller and Dürkes,[8] using the former author's procedure, investigated the conditions necessary for accuracy when widely varying quantities of sulphuric acid were employed. Among the sources of error in this investigation are: (*a*) solubility of benzidine sulphate; (*b*) occlusion of benzidine hydrochloride in the precipitated benzidine sulphate, both defects being common to all methods employing benzidine hydrochloride; (*c*) discrepancies arising from the acidity or alkalinity of the original sulphate containing solution, necessitating in certain cases a wide departure from standard conditions of estimation, the last point being peculiar to Müller's method. Certain modifications of this method were adopted by Talenti.[9]

Friedheim and Nydegger[10] adopted Raschig's method in principle. They found it impossible to get sufficiently accurate results with the solution Raschig advocated and they used an improved solution of benzidine hydrochloride (for details see later). Both the benzidine excess and the sulphate concentration were

[4] *Z. Angew Chem.*, 1903, **16**, 617.

[5] *Z. Angew Chem.*, 1903, **16**, 653.

[6] Ibid., 1903, **16**, 818.

[7] The solution employed is prepared as follows: (Compare *Analytical Chemistry*, Treadwell & Hall, Sixth Ed., Vol. II, 1924, 609), 40 g. benzidine are triturated with 40 ml. water, a further 750 ml. water and 50 ml. conc. hydrochloric acid are then added consecutively, the whole being diluted to 1 litre. For use the solution is diluted 20 times.

[8] *Z. Anal Chem.*, 1903, **42**, 477.

[9] *Giorn. Chim. Ind. Appl.*, 1926, **8**, 611.

[10] *Z. Angew Chem.*, 1907, **20**, 9; *Nydegger, Chem. Z.*, 1928, **52**, 318.

varied, the optimum conditions for the estimation of sulphate when present as sulphuric acid being ascertained. Bruckmiller,[11] working on similar lines to the above authors, employed a neutral sulphate solution and a definite percentage excess of benzidine hydrochloride. For concentrations of the SO_4 radicle varying from 35–1350 m.g. (approx.) per litre the error lay between —0·7 and + 0·3 per cent. Contrary to expectation the error, however, does not alter in a regular manner. Further, using a number of natural waters, Bruckmiller compared the results obtained in the estimation of sulphate by the benzidine method with those using barium chloride, but discrepancies up to ± 10 per cent. were observed.

The most recently published investigation of the subject is that of Haase.[12] To a large extent this work is a repetition of previous investigations, but here again the results do not appear consistent among themselves; for example, with increasing amounts of sulphate present as is shown in Table I., the percentage error does not follow a definite order :—

TABLE I.

Milligrams SO_3 Present. Per Litre.	Milligrams, SO_3 Found. Per Litre.	% Error.
9·70	4·20	—56·7
19·40	14·80	—23·7
29·10	26·85	— 7·74
38·75	34·80	—10·2
48·45	42·55	—12·2
58·15	53·75	— 7·06
67·85	64·55	— 5·07
77·75	76·55	— 1·21

It should be noted that the total reaction volume and the volume of precipitant employed were both kept constant, the only variable factor being the amount of sulphate. Incidentally, this author neglected apparently the filtrate, which contained information of outstanding importance with regard to the systematic errors of the estimation. Further, Haase investigated a new branch of the subject in determining the effect of varying quantities of calcium, magnesium, etc., on the estimation of sulphate. The conclusions at which Haase arrived are: (1) the benzidine hydrochloride method is applicable to the determination of sulphate in water; (2) the results compare favourably with the barium chloride method; (3) the benzidine hydrochloride method is much more rapid than the barium chloride method, for which reason it is well adapted to routine water analysis; (4) calcium chloride

[11] *Ind. Eng. Chem.*, 1915, **7**, 600.
[12] *Z. Angew Chem.*, 1927, **40**, 595; *Chem. Z.*, 1927, **51**, 637, 760.

in concentrations up to 50 D.H. gives rise to an error of only 3·2 per cent.; (5) magnesium sulphate exerts a solvent effect on benzidine sulphate even in small quantities. According to Haase[13] the detection of less than 30 m.g. of SO_3 per litre is not successful with Raschig's benzidine method, and with 30–70 m.g. of SO_3 per litre the error may be as high as 10 per cent. Raschig,[14] however, states that it is possible to detect as little as 3 m.g. of SO_3 per litre, the inherent difficulties such as solubility of benzidine sulphate, etc., being overcome by suitably concentrating the sulphate containing solution.

It is interesting to note that Vlastimil and Matula[15] obtained satisfactory results for the sulphate radicle in lead sulphate, using a slightly modified benzidine method. A modification of Raschig's method has also been employed by Testoni,[16] in which the end point of the titration is determined by the colour change of lead peroxide in the presence of benzidine. This is an excellent extension, but the method suffers from defects similar to those treated of in this investigation.

Experimental Method.

The work of Friedheim and Nydegger[17] resulted in their determining the optimum conditions for the estimation of the sulphate radicle in a solution of sulphuric acid, and these conditions were adhered to almost without modification in this investigation. Stated briefly the essential conditions are: (*a*) nature of the benzidine hydrochloride solution; (*b*) the sulphate ion concentration; (*c*) reaction volume.

The benzidine solution was prepared by dissolving 6·7 g. pure benzidine base in water with 20 ml. of conc. hydrochloric acid (sp. gr. 1·16), the solution being diluted to 1 litre with water. 1 ml. of this solution is equivalent to 0·00331 g. of SO_4 radicle, and its acidity with respect to hydrochloric acid is approximately 0·23 N. Of this solution a constant volume was taken in all experiments, namely, 120 ml.

For the sulphate containing solution Kahlbaum's analytically pure potassium sulphate was used, 17·2065 g. being dissolved and made up to 1 litre of solution, 1 ml. = 0·009485 g. SO_4. The quantity of sulphate radicle present was confirmed by an independent method. Suitable quantities of the solution, or of the solution appropriately diluted with distilled water, were employed.

[13] Loc. cit.
[14] *Z. Angew Chem.*, 1927, **40**, 864.
[15] *Chem. Z.*, 1926, **50**, 486.
[16] *Ann. Chim. Applicata*, 1928, **18**, 408.
[17] Loc. cit.

In all the following experiments the chief variable throughout the series was the amount of sulphate radicle. The total reaction volume was the same in each case, viz., 240 ml., the volume of the benzidine solution added being 120 ml. It follows that as the amount of sulphate radicle decreases the excess of benzidine hydrochloride correspondingly increases. Since one of the objects of the investigation was to standardise a rapid method for sulphate estimation in oil field waters, it is advisable to keep the volume of benzidine hydrochloride solution constant, rather than vary it in order to maintain a constant excess of benzidine hydrochloride in relation to the sulphate radicle present, as this would entail a double set of determinations.

The actual experimental procedure was to add to the sulphate solution diluted down to 120 ml. the requisite amount of benzidine hydrochloride solution, about 5 ml. at a time with constant stirring. After 10 minutes the precipitate of benzidine sulphate was poured on to a prepared filter, the filtration being aided by slight vacuum. A 2·3 c.m. diameter perforated disc, covered with two No. 42 Whatman filter papers of very slightly larger diameter, were used in a glass funnel of 6 c.m. diameter. About 20 ml. of the filtrate was found to be sufficient to transfer to the filter any benzidine sulphate remaining in the beaker, and finally the filter and precipitate were washed with 15 ml. of cold distilled water in 5 portions. After transference of precipitate, disc and filter paper to a beaker, together with 50 ml. water, the whole was titrated at about 50° with 0·1 *N* potassium hydroxide solution, using phenol phthalein as indicator. As the end point was reached the liquid was boiled for a few minutes and the titration completed. For strong concentrations of sulphate radicle the end point is rather difficult to detect unless at least 60–70 ml. of water are mixed with the precipitate. This point is apparently the solution of the difficulty experienced by Müller[18] in determining the end point when using Raschig's method for estimation.

In each case the sulphate radicle associated with soluble benzidine sulphate and any unprecipitated sulphate (refer to sulphate estimation in the presence of calcium) in the filtrate was estimated by means of the barium salt in the usual way.

Experimental Results in the Presence of the Potassium Ion.

On referring to Table II., which gives complete results of the various estimations carried out, the following points should be noted: (1) The reason for returning duplicates is to give a general idea of relative error in estimation. In no case does the titration

[18] Loc. cit.

TABLE II.

1. Amount of SO_4 present	0·2371	0·2371	0·2371*	0·2371*	0·1897	0·1897	0·09485	0·09485	0·07114	0·0
2. Amount of SO_4 determined by Benzidine	0·2395	0·2393	0·2387	0·2390	0·1908	0·1908	0·09476	0·09476	0·07041	0·0
3. Error in determination	+0·0024	+0·0022	+0·0016	+0·0019	+0·0011	+0·0011	—0·0009	—0·0009	—0·00073	—0·0
4. % Error	+1·01	+0·93	+0·68	+0·80	+0·58	+0·58	—0·09	—0·09	—1·03	—1·7
5. Sulphate determined in Filtrate by $BaCl_2$	0·0035	0·0035	0·0025	0·0026	0·0035	0·0037	0·0035	0·0035	0·0031	0·0
6. Volume of Filtrate and Washings ml.	360	360	380	380	300	300	320	320	420	
7. Solubility of $BaSO_4$ in above vol. (as SO_4)	0·0004	0·0004	0·0004	0·0004	0·0003	0·0003	0·0003	0·0003	0·0004	0·0
8. Total Sulphate in Filtrate	0·0039	0·0039	0·0029	0·0030	0·0038	0·0040	0·0038	0·0038	0·0035	0·0
9. Total Sulphate determined	0·2434	0·2432	0·2416	0·2420	0·1946	0·1948	0·09856	0·09856	0·07391	0·0
10. Total Sulphate present	0·2371	0·2371	0·2371	0·2371	0·1897	0·1897	0·09485	0·09485	0·07114	0·0
11. Nett Error	+0·0063	+0·0061	+0·0045	+0·0049	+0·0049	+0·0051	+0·00371	+0·00371	+0·00277	+0·0
12. Nett Error as % of SO_4 present	+2·66	+2·57	+1·90	+2·07	+2·58	+2·69	+3·91	+3·91	+3·89	+3·7

* These experiments were carried out by allowing the solution and precipitate to stand overnight before filtration. The results are consistent with

·07114	0·07114	0·04743	0·04743	0·02371	0·02371	0·009485	0·009485
·07041	0·06989	0·04607	0·04633	0·02146	0·02225	0·006020	0·005759
·00073	—0·00125	—0·00136	—0·00110	—0·00225	—0·00146	—0·003465	—0·003726
·03	—1·76	—2·87	—2·32	—9·49	—6·16	—36·53	—39·28
·0031	0·0035	0·0033	0·0038	0·0034	0·0033	0·0049	0·0059
420	420	400	400	420	420	450	450
·0004	0·0004	0·0004	0·0004	0·0004	0·0004	0·0004	0·0004
·0035	0·0039	0·0037	0·0042	0·0033	0·0037	0·0053	0·0063
·07391	0·07379	0·04977	0·05053	0·02526	0·02595	0·01132	0·012059
·07114	0·07114	0·04743	0·04743	0·02371	0·02371	0·009485	0·009485
·00277	+0·00265	+0·00234	+0·00310	+0·00155	+0·00224	+0·001835	+0·002574
·89	+3·73	+4·93	+6·54	+6·54	+9·45	+19·35	+27·14

nsistent with those obtained by using the normal procedure.

of benzidine sulphate by caustic potash vary for duplicates by more than 0·1 ml., but as the amount of sulphate present decreases the relative error correspondingly increases; (2) the experiments represent a gradually decreasing quantity of sulphate radicle; (3) the error in determination changes from + to — without irregularity. This change is due to solubility of benzidine sulphate remaining practically constant in the reaction volume while the amount of precipitate is steadily decreasing. Simultaneously an error occurs on account of occlusion; (4) the percentage error given in the 4th line increases to such proportions that the method is no longer practicable; (5) apart from minor irregularities due to experimental error, the amount of sulphate determined in the filtrate by barium chloride remains constant; (6) in lines 6 and 7 are given the volumes of filtrate and washings, and their respective content of dissolved barium sulphate in terms of SO_4[19] at 18°; (7) line 8 shows that the total sulphate in the filtrate is practically constant for all concentrations of the initial sulphate-containing solution; (8) the total sulphate determined is given in line 9, and comparison of these amounts with the total sulphate present (repeated in line 10) given as nett error (in line 11) shows that the amount of occlusion decreases steadily with decreasing sulphate concentration—a point which was to be expected.

In brief, the method is demonstrably practicable for all concentrations of SO_4 above 0·04743 g. in 120 ml., that is above 0·04 per cent. SO_4 radicle, but with the aid of the graph given in the figure the method holds down to our experimental limits—viz., 0·008 per cent. For solutions with concentrations above 0·2 per cent. the method can be applied upon appropriate dilution. The concentration of the potassium ion decreases from 0·16 to 0·006 per cent. pari passu with the decreasing quantity of sulphate radicle. Concordant results were obtained on using sulphuric acid instead of potassium sulphate for the sulphate ion concentration shown in the first four results (Table II.).

Experimental Method and Results in the Presence of the Calcium Ion.

It is of importance in connection with the analysis of oil field waters to ascertain the influence of calcium upon the determination. This influence is shown in Tables III., IV. and V.

The experimental procedure adopted was exactly similar to that described above, except that a definite volume of calcium chloride solution (made from Kahlbaum's calcium carbonate and hydrochloric acid and evaporation) was added to the sulphate solution

[19] Kohlrausch, *Z. Phys. Chem.*, 1904, **50**, 356.

TABLE III.

Amount of SO_4 present	0·2371	0·2371	0·2371	0·2371	0·2371	0·2371	0·2371	0·2371
Amount of Ca present	0·06990	0·06990	0·03495	0·03495	0·01398	0·01398	—	—
Amount of SO_4 determined by benzidine	0·2382	0·2382	0·2382	0·2382	0·2382	0·2382	0·2395	0·2393
Error in determination	+0·0011	+0·0011	+0·0011	+0·0011	+0·0011	—0·0011	+0·0024	+0·0022
% Error	+0·46	+0·46	+0·46	+0·46	+0·46	+0·46	+1·01	+0·928
Sulphate determined in Filtrate by $BaCl_2$	0·0043	0·0042	0·0023	0·0027	0·0023	0·0023	0·0035	0·0035
Vol. of Filtrate and washings ml.	430	430	390	390	430	430	360	360
Solubility of $BaSO_4$ in this volume (as SO_4)	0·0004	0·0004	0·0004	0·0004	0·0004	0·0004	0·0004	0·0004
Total Sulphate in Filtrate ..	0·0047	0·0046	0·0027	0·0031	0·0027	0·0027	0·0039	0·0039
Total Sulphate determined ..	0·2429	0·2428	0·2409	0·2413	0·2409	0·2409	0·2434	0·2432
Total Sulphate present	0·2371	0·2371	0·2371	0·2371	0·2371	0·2371	0·2371	0·2371
Nett Error	+0·0058	+0·0057	+0·0038	+0·0042	+0·0038	+0·0038	+0·0063	+0·0061
Nett Error, as % of SO_4 present ..	+2·45	+2·40	+1·60	+1·77	+1·60	+1·60	+2·66	+2·57
Amount of Ca present	0·06990	0·06990	0·03495	0·03495	0·01398	0·01398	—	—

TABLE IV.

Amount of SO_4 present ..	0·09485	0·09485	0·09485	0·09485	0·09485	0·09485	0·09485	0·09485
Amount of Ca present ..	0·06990	0·06990	0·03495	0·03495	0·01398	0·01398	—	—
Amount of SO_4 determined by benzidine	0·09162	0·09109	0·09266	0·09266	0·09319	0·09319	0·09476	0·09476
Error in determination ..	—0·00323	—0·00376	—0·00219	—0·00219	—0·00166	—0·00166	—0·0009	—0·0009
% Error	—3·41	—3·96	—2·31	—2·31	—1·75	—1·75	—0·09	—0·09
Sulphate determined in Filtrate by $BaCl_2$ ..	0·0059	0·0067	0·0044	0·0047	0·0051	0·0051	0·0035	0·0035
Vol. of Filtrate and Washings .. .. ml.	450	450	370	370	400	400	320	320
Solubility of $BaSO_4$ in this volume (as SO_4) ..	0·0004	0·0004	0·0004	0·0004	0·0004	0·0004	0·0003	0·0003
Total sulphate in Filtrate	0·0063	0·0071	0·0048	0·0051	0·0055	0·0055	0·0038	0·0038
Total Sulphate determined	0·09792	0·09819	0·09766	0·09796	0·09869	0·09869	0·09856	0·09856
Total Sulphate present ..	0·09485	0·09485	0·09485	0·09485	0·09485	0·09485	0·09485	0·09485
Nett Error	+0·00307	+0·00334	+0·00281	+0·00311	+0·00384	+0·00384	+0·00371	+0·00371
Nett Error as % of SO_4 present	+3·24	+3·52	+2·96	+3·28	+4·05	+4·05	+3·91	+3·91
Amount of Ca present ..	0·06990	0·06990	0·03495	0·03495	0·01398	0·01398	—	—

TABLE V.

Amount of SO_4 present ..	0·07114	0·07114	0·07114	0·07114	0·07114	0·07114	0·07114	0·07114
Amount of Ca present ..	0·06990	0·06990	0·03495	0·03495	0·01398	0·01398	—	—
Amount of SO_4 determined by benzidine	0·06675	0·06649	0·06780	0·06754	0·06858	0·06858	0·07041	0·06989
Error in determination ..	—0·00439	—0·00465	—0·00334	—0·00360	—0·00256	—0·00256	—0·00073	—0·00125
% Error	—6·17	—6·54	—4·70	—5·06	—3·60	—3·60	—1·03	—1·76
Sulphate determined in Filtrate by $BaCl_2$ ..	0·0063	0·0062	0·0053	0·0051	0·0044	0·0044	0·0031	0·0035
Vol. of Filtrate and Washings .. .. ml.	400	400	350	350	410	410	420	420
Solubility of $BaSO_4$ in this vol. (as SO_4)	0·0004	0·0004	0·0004	0·0004	0·0004	0·0004	0·0004	0·0004
Total Sulphate in Filtrate	0·0067	0·0066	0·0057	0·0055	0·0048	0·0048	0·0035	0·0039
Total Sulphate determined	0·07345	0·07309	0·07350	0·07304	0·07338	0·07338	0·07391	0·07379
Total Sulphate present ..	0·07114	0·07114	0·07114	0·07114	0·07114	0·07114	0·07114	0·07114
Nett Error	+0·00231	+0·00195	+0·00236	+0·00190	+0·00224	+0·00224	+0·00277	+0·00265
Nett Error, as % of SO_4 present	+3·25	+2·74	+3·32	+2·67	+3·15	+3·15	+3·89	+3·73
Amount of Ca present ..	0·06990	0·06990	0·03495	0·03495	0·01398	0·01398	—	—

before the addition of benzidine hydrochloride. Three different concentrations of calcium were used, as is shown in the Tables (line 2), and the effect of these on three different amounts of sulphate radicle was studied (Tables III., IV., V.). The upper limit of calcium ion concentration was such that the amount of calcium present in 120 ml. of sulphate solution was almost equal to the saturation point of the solution with regard to calcium sulphate; this volume dissolves approximately 0·07066 g. of calcium (in the form of $CaSO_4$) at 25°, whereas the actual amount used in the series of experiments was 0·0699 g. Ca. in 120 ml. The most concentrated sulphate solution employed corresponded with Friedheim and Nydegger's[20] optimum condition; the concentration yielding the smallest error in the foregoing investigation was made the second choice, whilst the third was the weakest concentration giving reasonably good results, viz., an error of about −1·5 per cent.

From the tables, which are self-explanatory, it will be seen that the presence of calcium chloride has only a slight effect on the determination, but that this effect increases with increasing calcium concentration. For low concentrations of sulphate, however, the effect becomes of great importance, as it renders the method impracticable with higher sulphate concentrations than is the case in the absence of calcium. The effect is such that the benzidine does not precipitate all the sulphate radicle, hence the results are lower than would otherwise be the case; in other words, the whole series of curves is moved towards the negative region. This is borne out by the fact that the estimation of sulphate in the filtrate by barium chloride is, in general, higher than in the absence of calcium. Further, the general trend of the results indicates that the higher the concentration of calcium the more sulphate is present in the filtrate.

Among the various explanations which may be put forward to account for this are the following: The solubility of benzidine sulphate may be enhanced by the presence of calcium chloride, due either to a solvent effect or to the formation of a soluble double salt of calcium sulphate (or chloride) and benzidine sulphate. It may be that unionised calcium sulphate is present, and as the calcium concentration increases the proportion of unionised calcium sulphate would also tend to increase; the results shown would thus be brought about, benzidine hydrochloride not effecting the necessary double decomposition. A further possibility is the occlusion of calcium sulphate in the precipitated benzidine sulphate; should this actually occur it must be more than compensated by

[20] Loc. cit.

the reverse phenomenon of unprecipitated sulphate in order to give the results obtained, since these display readings only slightly below values obtained in the absence of calcium. In short, the effect of calcium chloride solution on the determination is without appreciable effect, except when the concentration of sulphate ion is below 120 m.g. in 120 ml., that is 0·1 per cent. This is clearly shown on the accompanying graphs (Fig. 1).

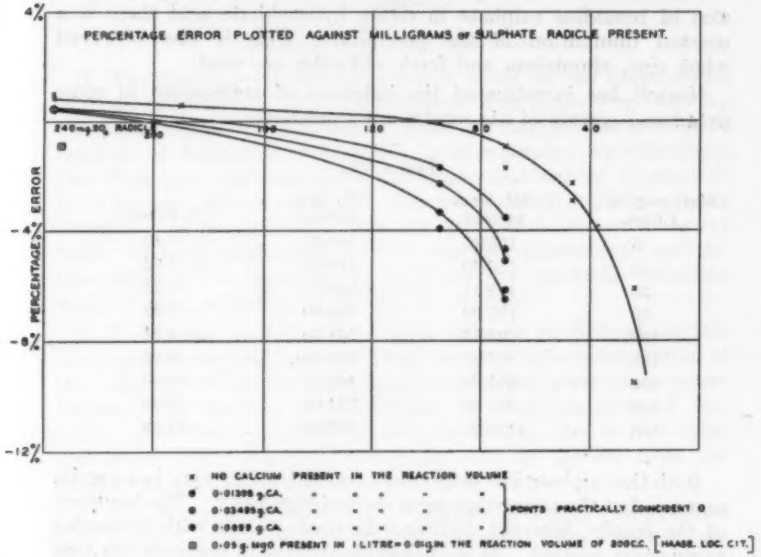

FIG. 1.

The three calcium curves obtained by plotting percentage error against sulphate present are similar to the parent curve for sulphate in the presence of the potassium ion. They are convex towards the axis of "milligrams of SO_4 present," cross the axis, and do not show any tendency within experimental range of becoming asymptotic to a constant error axis. Thus on the one side the negative error becomes infinite as the weight of sulphate present gives a benzidine sulphate precipitate approaching its solubility in the reaction volume, on the other side the occlusion effect exhibits an almost linear increase of the positive error. The curves show a general drift across the axis, the crossing of which indicates zero error. This crossing moves in the direction of increasing sulphate content, the curve for greatest calcium content crossing the axis

at the position of highest SO_4 concentration. As the calcium concentration decreases the curves approach the parent curve. A verticle line in any region through the curves give the variation in ± error for a definite sulphate radicle concentration.

Discrepancies Due to the Presence of Magnesium.

When a solution of magnesium chloride is added to a light suspension of benzidine sulphate in dilute hydrochloric acid there is a marked diminution of the precipitate. This is also observed when zinc, aluminium and ferric chlorides are used.

Haase[21] has investigated the influence of magnesium in some detail and certain of his results are appended.

Table VI.

MgO m.g. in 1 litre.	SO_3 m.g. present.	SO_3 m.g. found.	% Error.
5 ..	106·45 ..	106·25 ..	— 0·19
10 ..	116·40 ..	119·45 ..	+ 2·62
25 ..	146·15 ..	145·75 ..	— 0·27
50 ..	195·80 ..	194·00 ..	— 0·92
100 ..	296·15 ..	281·50 ..	— 4·94
150 ..	395·45 ..	366·00 ..	— 8·82
250 ..	691·60 ..	492·00 ..	—28·80
400 ..	981·60 ..	734·00 ..	—25·20
500 ..	1190·2 ..	782·00 ..	—34·29

Both the sulphate and magnesium concentrations vary in a regular manner, but the percentage error shows irregularity. The tendency of the results, however, indicates increasing error with increasing magnesium content. It is impossible strictly to compare our own results with the above since the concentrations employed differ widely. The following figures afford a rough comparison :—

Reaction volume.	SO_4 radicle present.	% Error.	
200	234·96 m.g.	—0·92	50 m.g. MgO present in 1 litre.
240	237·1	+0·5	81 m.g. CaO present in 1 litre.
240	237·1	+1·0	

It is clear, therefore, that the so-called solvent action of magnesium on benzidine sulphate is much more marked than is the case with calcium. Referring to the graph, it can be seen

[21] Loc. cit.

that for this concentration of magnesium the point lies on a curve well in the negative region; in fact, all the results, with one exception, given by Haase, are single points only on curves in the region of negative error. It may be that a double compound of benzidine sulphate and basic metallic sulphate or chloride or a double compound of benzidine and basic metallic sulphate, or a normal double compound is formed in the cases mentioned in this section, and these double compounds may be highly soluble.

Summary and Conclusion.

1. The literature of the subject lays stress on the great saving of time effected by using the benzidine hydrochloric method for the estimation of sulphuric acid. Raschig's modification of Müller's method of estimation, which has been extended by Friedheim and Nydegger, and employed by Haase and others, appears to have become general practice. This modification leads to greater simplicity in manipulation, but the method is not quantitative under all conditions owing to two opposing phenomena, namely, the occlusion of benzidine hydrochloric by insoluble benzidine sulphate and solubility of benzidine sulphate.

2. Under the particular conditions adhered to throughout this investigation the estimation is exact for only one concentration of the sulphate ion, the errors compensating at this particular concentration. The method is practicable for concentrations of SO_4 radicle above 0·04 per cent. without correction; below this value and above 0·008 per cent. corrections can be applied from the graphic record of the results.

3. The effect of the presence of calcium is slight, except when very small concentrations of SO_4 are present. This results in the method being practicable without correction only for concentrations of SO_4 above 0·06 per cent. (about 70 m.g. SO_4 in 120 ml.) in the presence of the maximum amount of calcium it is possible for this volume of solution to carry. The reason is probably the presence of unionised calcium sulphate, that is, calcium sulphate remaining undecomposed by the hydrochloric acid to form sulphuric acid.

4. Magnesium exerts a very marked solvent action on benzidine sulphate, even moderate concentrations vitiating the value of the estimation. The curves for magnesium lie well in the negative region of error, and crossing of the axis may not be realisable except for very high concentrations of sulphate. The solving of this difficulty resides in the removal of magnesium from solution by the usual analytical procedure.

PART II.—The Volumetric Estimation of Calcium in the Presence of Magnesium.

The determination of calcium when present alone is relatively simple, but when associated with other alkaline earths the problem becomes complicated. This applies particularly to magnesium with which calcium is commonly associated in oil field waters, dolomite and cements. It is necessary to know the exact calcium content in each case. The volumetric method of estimation is undoubtedly the most convenient both from saving of time and ease of manipulation. Many suggestions have been put forward in the literature at various times regarding this volumetric estimation, but it was found that without reprecipitation discrepancies arose when much less than the tolerated magnesium content[22] was present. Under these conditions magnesium oxalate is occluded in the precipitate of calcium oxalate.[23] Owing to the low solubility of magnesium oxalate, namely 0·3 g. in 1 litre water, 18°,[24] it is practically impossible to remove this satisfactorily without reprecipitation. The object of the present experiments was to determine the maximum proportion of magnesium to calcium which can be present without rendering reprecipitation necessary, and also to decide on the best procedure to be adopted when that proportion is exceeded.

Method of Investigation.

In the following experiments the proportion of magnesium to calcium (by weight) was varied between the limits of 10 Ca : 1 Mg. and 10 Ca : 100 Mg., the reaction volume being kept constant at 200 ml.; calcium and magnesium both were in the form of chlorides. The actual determination for these proportions was then carried out by each of two methods, precipitation of calcium oxalate in alkaline solution and precipitation in acid solution.

Alkaline Precipitation.—Sufficient ammonium chloride was added to prevent the later precipitation of magnesium hydroxide, followed by excess of ammonia and the solution brought to boiling point. Excess of a N. Sol. of ammonium oxalate was introduced and the whole allowed to stand for 1 hour. The precipitate was then filtered off and washed with hot water.

Acid Precipitation.—The procedure recommended in "Analytical Chemistry," Treadwell and Hall,[25] was followed, the weight of calcium present in 200 ml. being 0·1 g., which was within Treadwell's experimental limits for calcium.

[22] 10 Mg. : 1 Ca. Blasdale, *J. Amer. Chem. Soc.*, 1909, **31**, 917.
[23] Richards, *Z. Anorg. Chem.*, 1901, **28**, 71.
[24] Kohlrausch, *Z. Phys. Chem.*, 1905, **50**, 356.
[25] Sixth Edition, 1924, Vol. II, 86.

Both these methods gave similar results for each concentration of magnesium; in other words, the method of single precipitation broke down with both at the same Ca : Mg. proportions.

Reprecipitation Method.—Without puncturing the filter paper the mixed oxalate precipitate is treated alternately with small quantities of hot dilute hydrochloric acid and hot water, the total volume of the solution being kept as small as possible when magnesium is to be estimated subsequently. The filtrate containing the dissolved oxalates is brought to boiling, excess of ammonium hydroxide and 5 ml. N. ammonium oxalate solution added. The precipitate is kept hot, allowed to stand ¾ hour, filtered and washed.

The precipitate and filter paper were treated in accordance with directions given,[26] except that the filter paper was submerged in the liquid throughout the titration. On account of this procedure a correction of 0·10 ml. of 0·1 N potassium permanganate was deducted from the titration.

Two precipitations were run concurrently for each experiment; in one the calcium was precipitated in alkaline solution, in the other in acid solution. The success of either method was readily seen by the ease of freeing the precipitate from occluded magnesium oxalate by washing. Any of the latter remaining would give a high calcium result and corresponding low magnesium value.

It was found (see Table VII.) that for all proportions of magnesium to calcium in excess of 1 : 1 the ordinary methods of precipitation

TABLE VII.

Table Showing the Effect of Varying Concentrations of Magnesium on the Volumetric Estimation of Calcium.

Proportion Mg. : Ca.	Ca present in grams.	Ca estimated in acid sol.	Ca estimated in alkaline sol.	
No Mg. ..	0·1001	0·0985	0·0983	To determine order of experimental error.
1 Mg. : 10 Ca.	0·09092	0·09094	0·09122	
1 Mg. : 1 Ca.	0·09092	0·09152	0·09152	
15 Mg. : 1 Ca.	0·1001	No result.	0·1067	The error in alkaline solution even after washing with 1½ litres hot water is too high for analytical work.
2 Mg. : 1 Ca.	0·1001	No result.	No result.	Impossible to wash free from soluble oxalate.
5 Mg. : 1 Ca.	0·1001	,,	,,	
10 Mg. : 1 Ca.	0·1001	,,	,,	
No Mg. ..	0·1001	0·0981	0·0986	Reprecipitated to determine error involved.
2.5 Mg. : 1 Ca	0·1001	—	0·1001	Reprecipitated.
5 Mg. : 1 Ca.	0·09092	0·0898	0·0898	,,
10 Mg. : 1 Ca.	0·09092	0·0893	*0·0829	,,

* Dilute sulphuric acid used for dissolving the mixed oxalates. In other cases dilute hydrochloric acid was employed.

[26] Applied Inorg. Analysis, Hillebrand and Lundell, 1929, 502.

gave rise to occluded magnesium oxalate which was impossible to remove by washing. Both methods were found to break down between 1·0—1·5 Mg. : 1 Ca. In all cases of greater proportion of magnesium it is necessary therefore to reprecipitate.

With regard to the comparative values of precipitation in alkaline solution and precipitation in acid solution, it was found that there was no marked advantage in either, but that precipitation in acid solution, while taking longer time, gives slightly better results for calcium when the proportion of Mg. : Ca is in the region of 10 : 1. For lower proportions precipitation in alkaline solution is much quicker and is quite accurate.

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Hydrogenation of Estonian Oil Shale and Shale Oil.*

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Introduction.

The study of the chemical constitution of organic matter or kerogen of oil shales is undoubtedly connected with the problem of solubility of kerogen in inert solvents.

The experiments on solubility, carried out by one of the authors[1], showed that the kerogen of "kukersite," as the oil shale is called, is practically insoluble in inert solvents, *e.g.*, ethyl alcohol, acetone, ether, chloroform, benzene, carbon disulphide, toluene and xylene. Even the extraction of kukersite with benzene under pressure at about 250° C. yields only about 1 per cent. of extract.[2]

On the other hand, the kerogen is easily decomposed and depolymerised by heat, but the decomposition proceeds too far on distillation of the mineral under atmospheric pressure, and a considerable amount of the carbon is obtained in the form of coke.[3]

The distillation of the shale *in vacuo* decreases the amount of coke, but cannot eliminate entirely the coke formation. As is shown in the present paper, on hydrogenation practically all organic matter of kukersite is converted into gaseous and liquid products and a *soluble residue*. Therefore, besides its practical importance, hydrogenation opens a new possibility for studying the nature of kerogen.

For comparison three series of experiments were carried out :— (i.) heating of the shale under pressure of water vapour ; (ii.) heating under pressure of hydrogen ; and (iii.) heating under nitrogen pressure. The hydrogenation of shale oil has been studied as well.

The Composition of the Raw Material.

The shale contained 1·6 per cent. of moisture, 40·2 per cent. of ash, and 58·2 per cent. of organic matter.

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* Paper received January 19, 1932.

[1] *P. N. Kogerman*, "The Chemical Composition of the Estonian M.. Ordovician Oil-bearing Mineral "Kukersite." *Acta et Comment. Univers-Dorpat*, A. III, 6, 1922.

[2] *A. Schneider*, "Gesammelte Abhandlungen zur Kenntnis der Kohle," 1922, **5**, 41.

[3] Compare *P. N. Kogerman*, "The Present Status of the Oil-Shale Industry in Estonia," *J.I.P.T.*, 1925, **11**, 221.

Procedure.

The experiments were carried out in a revolving, gas-heated, autoclave, made of special steel, having a capacity of about 900 ml. The autoclave was provided with a manometer and a nitrogen-filled mercury thermometer. Charges of shale taken: 200–300 grams. In some experiments 5 per cent. of iron oxide was added to the shale. After about 60–90 mins. a temperature of 370–410° C. was reached, at which temperature the heating was continued for one to two hours. Care was taken to keep the conditions of the operation, *e.g.*, the rate of heating, uniform in all the experiments.

Part I.

Pyrolysis of Kukersite under a Pressure of Water Vapour.

In this series of experiments about 50 g. of water was added to the shale in the autoclave before starting the experiment. During the reaction a maximum pressure of 190–287 kg./sq. cm. was developed. At the end of the experiment, after cooling, the manometer still showed a pressure of 20–30 atmospheres, *i.e.*, about 20 litres of gas was formed on pyrolysis. (See Fig. 1.)

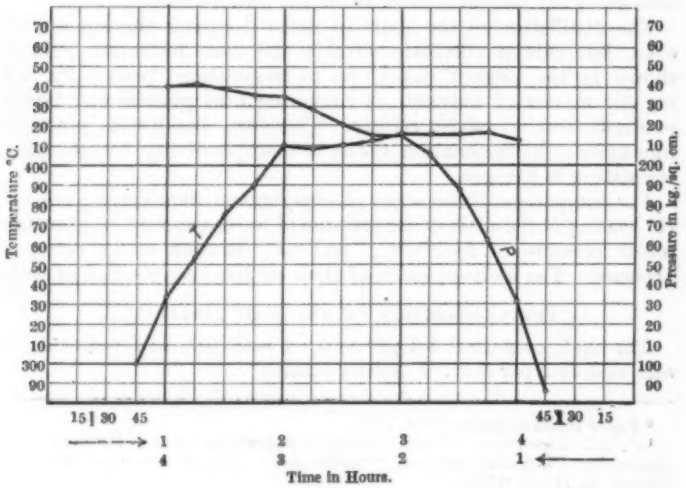

Fig. 1.

PRESSURE-TEMPERATURE CURVES: P—PRESSURE; T—TEMPERATURE. THERMAL DECOMPOSITION OF SHALE UNDER A PRESSURE OF WATER VAPOUR.

The particulars of the experiments are given in Table I., which shows the yield of liquid products as well :—

TABLE I.

The Results of Pyrolysis of Kukersite under a Pressure of Water Vapour.

Nos. of Experiment.	Charges in g.	Catalyst.	Pressure in kg/sq. cm.		Reaction temp. °C.	Duration in hours.	Oil, b.p. up to 170° C.	
			Max. pressure.	Final pressure.			Oil in g.	Per cent. of oil based on shale.
1	300	Fe_2O_3	259	34	390–400	1½	23·0	7·7
2	300	,,	242	30	370–380	1	23·0	7·7
3	300	,,	210	27	380–390	1	23·0	7·7
4	300	,,	165	22	380–390	½	20·0	6·7
5	300	,,	187	22	380–390	½	19·0	6·3
7	200	,,	192	18	375–385	2	16·0	8·0
8	200	,,	240	28	400–405	2	21·0	10·5
9	200	none	232	27	400–406	2	23·0	11·5
10	300	,,	287	34	390–402	2	32·0	10·7

THE PRODUCTS OF PYROLYSIS.

(1) *Gases.* — The gases were analysed in a modified *Orsat-apparatus :* methane, ethane and hydrogen were determined by partial combustion over CuO in a quartz-tube. The gases contained chiefly saturated hydrocarbons and carbon dioxide.

As an example, the analysis of gases obtained in experiment No. 3 (see Table I.) is given : $CO_2 + H_2S$, 38·4 per cent. ; C_nH_m, 1·0 per cent. ; O_2, 0·2 per cent. ; CO, 0·5 per cent. ; H_2, 9·6 per cent. ; CH_4, 21·7 per cent. ; C_2H_6, 22·5 per cent. ; N_2, by diff., 6·1 per cent.

(2) *Liquid products.*—The products of the pyrolysis which remained in the autoclave formed a mixture of a yellowish-brown oil and a brown asphalt-like sticky substance. The mixture was distilled in a copper vessel, provided with a long Liebig condenser. Up to 170° C. water and light oil passed over. This was called the *gasoline-fraction.*

The yield of gasoline is dependent upon the temperature and duration of the process ; *e.g.*, on heating of the shale at 375–380° C. for two hours the yield of gasoline fraction was 8 per cent. ; heating at 400–410° C. for the same period increased the yield of gasoline to 10 to 11 per cent. (based on the weight of the shale).

The residue, which remained in the still boiling above 170° C. appeared as a black solid substance. About 30 to 40 per cent. of it was soluble in ether. The coke formation has advanced too far and the residue did not soften on heating.

The gasoline fraction.—The freshly distilled gasoline was almost water-white, but darkened on standing. After treatment with 10 per cent. NaOH solution and dilute sulphuric acid, the fraction

was dried and redistilled. The refined product remained water-white on standing.

The gasoline was refractionated, and the following fractions taken :—60–120° C., 120–150° C., and 150–190° C. The properties of these fractions are given in the Table II. below :—

TABLE II.

Properties of Light Oils.

Fraction °C.	Sp. Gravity at 20° C.	Refract. indices (Abbé Refractometer).
60–120° ..	0·7137 ..	1·4018 (at 20°)
120–150° ..	0·7848 ..	1·4357 (at 14°)
150–190° ..	0·8073 ..	1·4499 (at 14°)

As regards the effect of ferric oxide upon the process of pyrolysis, definite conclusions cannot be drawn; undoubtedly iron combines with sulphur, and the sulphur content of the oils is reduced as had been found in some experiments.

PART II.

PYROLYSIS OF KUKERSITE UNDER PRESSURES OF NITROGEN AND HYDROGEN.

The shale used for this series of experiments had the following composition: moisture, 1·7 per cent.; total ash, 50·9 per cent., and organic matter, 47·4 per cent.

The procedure remained essentially the same as described in the introduction. Charges taken about 300 grams, and 5 per cent. of iron oxide was added to the shale. The products of pyrolysis resembled the products described in Part I., but in the case of nitrogen the inner surface (walls) of the autoclave was covered with a very sticky asphalt-like substance.

During the reaction, at a fairly constant temperature, the nitrogen pressure curve showed a tendency to rise. As an example, comparative yields of oil from the shale under nitrogen and hydrogen pressures are given in Table III. below :—

TABLE III.

Yield of Oil on Pyrolysis of Shale.

Experiment.	Total amount of shale treated in g.	Gas used.	Liquid products boiling up to 275° C. under 15 mm. pressure; per cent. based on the shale.			Remarks.
			Oil.	Water.	Total.	
1 1a	620	N_2	23·9	4·2	28·1	Mean figures of two experiments are given.
2 2a	645	H_2	30·5	4·0	34·5	
3 3a	628	twice treated under H_2.	29·2	4·1	33·3	

In the experiments 3 and 3A the shale was heated under hydrogen pressure, then, after cooling, the gases released and the product hydrogenated once more.

The gas from experiments with nitrogen had the following composition (Expmt. 1a): CO_2, 7·9 per cent.; C_nH_{2n}, 0·3 per cent.; O_2, 0·0 per cent.; H_2, 1·8 per cent.; CO, 2·7 per cent.; $CH_4+C_2H_6$, 5·6 per cent. and N_2, 81·7 per cent.

The products of pyrolysis, liquid and solid, were introduced into a 2-litre copper flask and fractionated: up to 170° C. under atmospheric pressure, above that temperature under 15 mm. Hg. pressure. With the first fraction water passed over as well. The results of fractionation are given in Table IV.:—

TABLE IV.

Fractionation of Oils.

Experiments.	Percentage yield of Fractions. 1 and 1a.		2 and 2a.		3 and 3a.	
Fractions ° C.	On organic matter.	On the oil.	On organic matter.	On the oil.	On organic matter.	On the oil.
Up to 170 at atm. ..	18·1	35·8	22·3	34·7	21·2	33·4
„ 125 at 15 mm.	6·1	12·2	9·9	15·3	10·3	16·9
125-155 „ ..	6·0	11·9	8·3	12·9	7·3	11·8
155-185 „ ..	5·5	10·9	8·1	12·5	8·5	13·8
185-215 „ ..	4·5	8·0	6·6	10·3	4·6	7·5
215-265 „ ..	—	—	—	—	9·9	15·9
215-270 „ ..	—	—	9·2	14·2	—	—
215-275 „ ..	10·6	21·0	—	—	—	—
Total yield ..	50·8	99·8	64·4	99·8	61·8	99·3

Comparing the results of conversion of kerogen into oils (Table IV.), one can see that, on "hydrogenation," about 10 per cent. more of organic matter is converted into oils than on treatment under nitrogen pressure. In order to check some of the previous results, three experiments were carried out under strictly comparable conditions:—

(i.) The autoclave, without shale, was filled with hydrogen up to an initial pressure of 106 kg./sq. cm. and heated at 395–407° C. for 1½ hours. (Blank experiment.)

(ii.) 250 g. of shale was introduced into the apparatus, then hydrogen fed in up to 98 kg./sq. cm. of initial pressure, and the shale heated at 394–410° C. for 2½ hours.

(iii.) 250 g. of shale of the same quality was heated in the autoclave under nitrogen pressure at 398–411° for 2½ hours. Initial pressure of N_2 was 97 kg./sq. cm.

The rate of heating in experiments (ii.) and (iii.) was the same. The temperature and pressure were recorded every 10 mins., and temperature-pressure curves are given in Fig. 2.

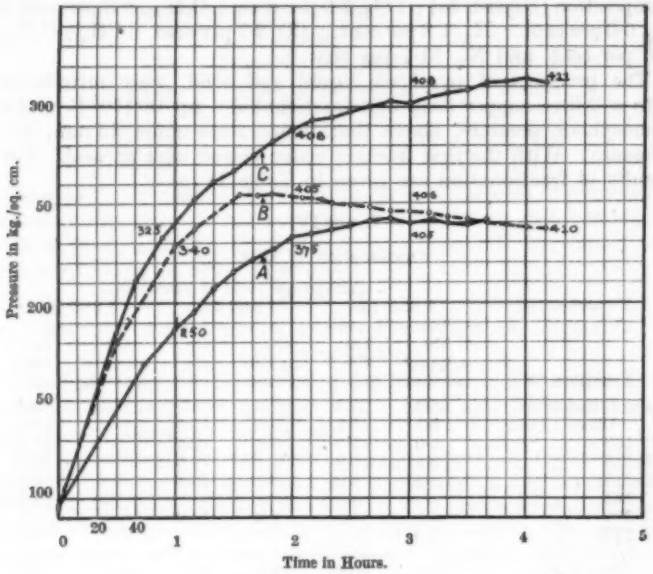

FIG. 2.

TYPICAL PRESSURE-DECOMPOSITION CURVES: A—BLANK EXPERIMENT; B—HYDROGENATION CURVE; C—THERMAL DECOMPOSITION UNDER NITROGEN PRESSURE. THE FIGURES ON THE CURVES REFER TO TEMPERATURES.

In the blank experiment the pressure of gas rises with the temperature and remains constant at constant temperature. After cooling, the manometer showed a pressure of 105 atmospheres—*i.e.*, one atmosphere less than the initial pressure. Although the autoclave proved to be gastight, there might have been some losses on heating at higher temperatures and pressures. Another reason for this discrepancy might be the inaccuracy of readings, because one point of the manometer corresponds to 20 kg./sq. cm.

In the second experiment (hydrogenation) the pressure curve began to fall as soon as the reaction temperature was kept constant. After cooling of the apparatus the manometer showed a pressure of 74 kg./sq. cm.—*i.e.*, 24 kg./sq. cm. less than the initial pressure.

During the third experiment, when the shale was treated under pressure of nitrogen, the pressure curve was steadily rising, although the temperature was kept constant. The final pressure at room temperature exceeded the initial pressure by 8 atmospheres.

Analysis of gases.—The analysis of gases obtained on pyrolysis of the shale under hydrogen (E. 2) and nitrogen pressures (E. 3) are given in Table V. below :—

TABLE V.

Analysis of Gases.

Gas.	Expmt. 2.	Expmt. 3.
CO_2 ..	4·8%	4·9%
C_nH_{2n} ..	0·3	0·2
O_2 ..	0·0	0·1
CO ..	1·4	0·2
H_2 ..	86·2	1·3
C_2H_6 ..	0·8	2·4
CH_4 ..	2·6	1·4
N ..	3·9	89·5
	100·0	100·0

Liquid Products.—The liquid products of both experiments were distilled in a copper vessel of about 750 ml. capacity. The oil was separated from water, treated with soda solution, then washed with very dilute sulphuric acid and water. The neutral oil was dried over fused sodium sulphate and fractionated under atmospheric pressure.

The light fractions of the oils seem to be very similar in composition, as is evident from the Table VI. below :—

TABLE VI.

Properties of Oils.

Oil.	Fraction °C.	Sp. Gravity at 20° C.	Mean Mol. weight.	Refractive index.
From E.2 : hydrogen pressure	95–160	0·7455	111	1·4167
From E.3 : nitrogen pressure..	95–160	0·7453	109	1·4179

The water obtained on pyrolysis of the shale showed an acid reaction. The oil boiling up to 160° C. showed a marked solubility in 10 per cent. solution of sodium hydroxide.

PART III.

EFFECT OF HYDROGENATION UPON THE FORMATION OF "FREE CARBON" AND UPON THE SOLUBILITY OF THE RESIDUE.

The product of hydrogenation of the shale is a very viscous, pasty substance with a characteristic smell of kerosine. The

residue remaining in the distillation flask after removal of light oils, forms a soft brownish-black asphalt-like substance. Its penetration values at 25° C. were 94–128, dependent upon the conditions of the experiments.

For the determination of "free carbon" or "coke" in the residue, the latter was extracted with benzene for about 16 hours. The ash contents of the residue was determined in an electric furnace, and CO_2 in Baur's apparatus. Mineral ash $+CO_2$ = total ash.

The difference between the percentage of organic matter in the residue (*a*) and that of the portion soluble in benzene (*b*) is regarded here as percentage of "coke" (*a*-*b*).

The percentage of coke in the residue is dependent upon the temperature of the reaction, pressure of hydrogen, and duration of the experiment.

In Table VII. the particulars of the experiments and percentages of coke in residue are given.

The highest percentage of coke was formed on heating the shale without hydrogen (blank experiment No. 20)—*i.e.*, 20·4 per cent. of the residue.

At temperatures below the "transition interval"—*i.e.*, 360–390° C.—at which the insoluble kerogen is converted into a soluble semi-solid intermediate substance, the "coke" contains undoubtedly a part of unaltered kerogen as well. Below the transition temperature, the decomposition respectively depolymerisation of the kerogen is very slow (experiment No. 6).

On heating the shale at temperatures between 380–410° C. under hydrogen pressure of 250 kg/sq. cm. for 2–3 hours, practically *no coke is formed.*

Above this range of temperature—*e.g.*, 440–450° C.—the secondary decomposition or "cracking" of the intermediate product begins, and the coke contents of the residue increases again.

In hydrogenation we have a new method for studying the nature of the kerogen. Of all the methods applied so far as for coal and shale research, none gives the bulk of kerogen in soluble form. How far the salts of organic acids, a fair percentage of which the kerogen probably contains, affect the transition temperature is difficult to tell at present. But, on the other hand, the transition interval excludes the presence of many aliphatic and particularly aromatic acids[4], and gives some hints for searching for oxygen-compounds in the shale oil.

[4] Compare: Hurd, C. D., "The Pyrolysis of Carbon Compounds," New York, 1929, pp. 475-523.

TABLE VII.

TABLE VII.

Yields of Oils and Analysis of Residues obtained on hydrogenation of Kukersite: For each experiment 300 g. of shale, containing 58·2% or 174·6 g. of organic matter was taken.

No. of Experiment.	Catalyst.	Hydrogen pressure kg./sq. cm.				Reaction Temperature ° C.	Duration hrs.	Fraction up to 170°C./ atm. Gasoline fraction.				Fraction b.p. 60-170°C/10 mm Hg. Kerosine fraction.		Residue.						
		Initial a.	Maximum.	Final c.	Difference a-c.			Water g.	Oil g.	Per cent. of oil based on shale.	Per cent. of oil based on organic matter.	Per cent. of oil based on shale.	Per cent. of oil based on organic matter.	Distillation limit.*	Residue g.	Per cent. of soluble bitumen based on residue.	Per cent. of coke based on residue.	Per cent. of mineral ash based on residue.	CO_2 in %.	Per cent. of bitumen based on organic matter.
1.	Fe_2O_3*	80	194	42	38	400–410	2·5	8·0	25·0	8·3	14·8	—	—	—	—	—	—	—	—	—
2.	Fe_2O_3	85	222	50	35	400–410	1·75	17·0	32·0	10·7	18·9	14·7	26	162° C./10mm.Hg.	—	34·9	3·4	50·1	11·6	—
3.	,,	90	235	48	42	400–410	3·25	16·5	35·5	11·8	21·0	10·5	18·7	125	,,	—	33·9	3·7	51·1	11·2	—
4.	None	85	223	52	33	400–410	2·0	14·0	31·0	10·3	18·4	13·5	24·	130	,,	—	31·4	6·4	49·8	12·4	—
5.	,,	90	198	87	3	340–350	2·5	10·5	4·5	1·5	2·7	1·4	2·7	150	,,	—	27·8	32·5	32·6	7·1	—
6.	,,	85	218	57	28	380–390	3·0	13·0	26·2	8·7	15·0	12·3	21·2	170	,,	—	38·2	0·0	46·2	15·6	—
7.	,,	92	250	49	43	420–430	2·75	13·5	39·0	13·0	22·3	14·4	24·7	185	,,	156	23·8	2·3	55·2	18·7	68·2
8.	Iron cubes of 1 cm^3	95	260	58	37	400–410	3·0	13·0	32·4	10·8	18·5	14·0	24·0	170	,,	170	32·8	0·0	49·3	18·6	74·4
9.	,,	94	250	48	46	440–450	2·5	12·0	37·5	12·5	21·5	2·5	4·2	170	,,	—	27·8	6·9	52·2	13·1	—
10.	,,	93	260	60	33	400–410	3·0	13·5	34·9	11·6	20·0	17·4	29·9	185	,,	158	21·5	8·0	54·7	15·8	69·3
11.	,,	93	243	50	43	400–410	3·25	13·5	34·6	11·5	19·8	16·9	29·0	175	,,	159	27·4	4·9	49·3	14·1	73·3
12.	None	87	241	55	32	400–410	3·0	13·9	33·0	11·0	18·9	16·4	28·3	175	,,	173	35·8	0·8	49·8	13·6	82·4
13.	,,	98	260	60	38	400–410	3·25	13·5	34·3	11·4	19·7	18·0	31·0	180	,,	168	29·4	0·0	53·5	17·1	79·0
14.	,,	93	240	62	31	380–390	3·25	13·6	26·0	8·7	14·9	17·1	29·4	185	,,	183	31·9	0·2	51·8	16·1	77·7
15.	,,	96	260	54	42	420–430	2·75	13·5	40·4	13·5	23·2	16·8	28·9	170	,,	152	20·8	0·7	60·9	17·6	85·5
16.	,,	47	173	38	9	400–410	3·25	12·0	33·3	11·1	19·1	12	20·6	—	,,	182	—	—	—	—	—
17.	,,	52	180	37	15	400–410	3·0	12·5	34·8	11·6	19·9	13·1	22·5	170	,,	179	32·3	4·8	49·1	13·7	—
18.	,,	92	225	75	17	370–380	2·75	11·3	10·3	3·4	5·9	5·6	9·6	185	,,	243	54·5	4·0	33·1	8·5	—
19.	,,	0	153	29	–29	400–410	2·5	13·0	28·5	9·5	16·3	8·5	14·5	170	,,	183	15·1	20·4	47·4	17·0	46·6
20.	,,	82	213	73	9	380–390	1·0	11·0	9·6	3·2	5·5	5·1	8·8	170	,,	241	51·5	4·8	32·8	10·9	85·3
21.	,,	86	222	51	35	380–390	5·0	12·6	26·2	8·7	15·0	13·7	23·6	170	,,	191	38·6	0·1	45·9	15·4	80·8
22.	,,	85	235	71	14	400–410	1·0	12·0	19·5	6·5	11·2	10·2	17·6	170	,,	207	43·1	3·2	40·2	13·5	79·9
23.	,,	84	235	51	33	400–410	5·0	12·6	34·0	11·3	19·5	15·4	26·5	170	,,	174	35·6	1·3	49·7	13·4	81·2

* The "Distillation limit" is regarded as the temperature up to which the oils have been removed from the hydrogenated product.

As an average the hydrogenation product of the kerogen contained :—

About 12 per cent. of gasoline fraction, b.pt. below 170° C.

About 17 per cent. of kerosine fraction, b.pt. 60–170° C. at 10 mm. Hg.

About 20 per cent. of asphalt.

Percentage based on dry shale.

The kerosine fraction contains about 13 per cent. of higher phenols, 32 per cent. of unsaturated and 8·5 per cent. of aromatic compounds.

The yield of oils produced from the shale on treatment under hydrogen pressure in one run does not surpass to any considerable extent the yield of oils, obtainable on distillation under ordinary pressure.

Part IV.

Hydrogenation of Shale Oils.

For hydrogenation the following shale oils were taken :—

(i.) Crude shale oil, obtained from Kohtla plant[5]; sp. gravity about 1·00.

(ii.) A fraction of this oil, boiling from 170° C. at atm. pressure up to 215° C. at 15 mm.

(iii.) The residue boiling above 215° C. at 15 mm.

(iv.) The neutral shale oil, obtained from the crude oil on removal of acidic constituents (phenols and acids).

(v.) Crude phenols, obtained on soda-wash of the crude oil.

Charges taken : 300–350 grams. Initial pressure of hydrogen was about 100 atmospheres. Reaction temperature : 400–410° C., and duration of reaction 90–150 mins.

The temperature-pressure curves were similar to those obtained on hydrogenation of the shale.

The products of hydrogenation were distilled in a round-bottom flask, provided with a Liebig condenser, and five fractions were taken—*i.e.*, one up to 170° C./atm. and four under 15 mm. Hg. pressure.

The particulars of these experiments are given in Table VIII.

In the experiment No. 17, the crude oil was twice treated under hydrogen pressure.

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[5] For particulars, see : *P. Kogerman*, "Oil Shale Industry in Estonia," *J.I.P.T.*, 1925, **11**, 221-222, and by the same author, "On the Chemistry of the Estonian Oil Shale 'Kukersite,' Archiv für die Naturkunde Estlands," 1931, 1. Ser., 10, Bd., 2 Lief.

TABLE VIII.

Results of Fractionation of Hydrogenated Shale Oils.

No. of Experiment.	Oil.	Catalyst.	Specific gravity at 20°C.		Fraction up to 170°/atm.; % by weight.			Fractions under 15 mm. pressure; % by weight.	
			Original oil.	Hydrogenated oil.	Water.	Oil.	Total.	60°-215°.	Residue per cent
1	Crude oil	None	—	—	1·4	6·8	8·2	36·9	54·5
4		5% Fe_2O_3	1·000	0·957	1·8	14·7	16·5	44·3	37·8
5		Fire clay	—	—	2·3	9·8	12·1	44·8	—
17		5% Fe_2O_3	1·000	0·945	1·5	14·6	16·1	44·6	—
7	Fraction b. pt. 170° C. at atm. press. to 215° C. at 13 mm.	None	—	—	0·8	9·1	9·9	66·7	22·5
8		5% Fe_2O_3	0·954	0·912	0·4	11·4	11·8	72·4	15·7
13	Neutral oil	5% Fe_2O_3	—	—	—	7·1	7·1	42·3	49·7
11	Residue	Fe_2O_3	—	—	1·3	3·5	4·8	17·6	—
18	Crude phenols	13% Fe_2O_3	—	—	4·7	24·3	29·0	—	—

The results of experiments on the desulphurisation of shale gasoline by hydrogenation have been published elsewhere[6], and show that on hydrogenation the complete desulphurisation of shale petrols is achieved.

The results of hydrogenation of Estonian shale oils can be summarised as follows:—

(1) On hydrogenation of shale oils, with the formation of light oil, polymerisation occurs with the formation of heavier, higher boiling oils. (Compare experiments Nos. 7 and 8.) For instance, the fraction of oil boiling between 170° C. and 215° C. at 15 mm. yielded, after hydrogenation, 11·4 per cent. of oil boiling below 170° C., and about 17 per cent. of residue boiling above 215° C, at 15 mm.

(2) The crude phenols, boiling above 170° C., yielded 24·3 per cent. of light oil and 4·7 per cent. of water.

(3) The residue obtained on distillation of the crude oil, from which all constituents boiling below 215° C. at 15 mm. had been removed, yielded, on hydrogenation at 380° C., 4·8 per cent. of light oil. At higher reaction temperatures—*e.g.*, 427° C.—the coke formation advanced too far.

(4) The lower boiling fractions of oils, obtained on hydrogenation of crude shale oil, were almost identical with those obtained on hydrogenation of the shale.[7]

General Summary and Conclusions.

(1) The amount of kerogen of the shale liquefied on hydrogenation in one run does not exceed to any considerable extent the amount of liquid products obtained by ordinary distillation.[8]

(2) On hydrogenation of kukersite an absorption of hydrogen is observed: about 1·8 per cent. by weight of kerogen. Below

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[6] Paul N. Kogerman, *J. Inst. Fuel.*, 1932, **5**, 278.

[7] After this paper had been written, a paper on cracking and hydrogenation of shale oils was published by Tilicheev and Seledgeev ("Oil Shales and their Technical Utilisation," Leningrad, 1932, pp. 449-481; in Russian). The authors claim that on "repeated" or total hydrogenation of Estonian shale oil about 70 per cent. of gasoline, *i.e.*, oil boiling below 200° C., is obtained. Their procedure was: after each run (experiment) the light fraction, boiling up to 200° C., was distilled off, and the residue treated again under hydrogen pressure. Initial pressure of hydrogen about 200 atms., reaction temp. about 450° C.; duration: first run 3 hrs., second and third 6 hrs. each. Ten per cent. of nickel oxide was used as catalyst.

Compare also: H. I. Waterman, S. C. de Jong and A. J. Tulleners' "Contribution to the Knowledge of the Treatment of Estonian Oil-Shale," *J.I.P.T.*, 1932, **18**, 183-186.

[8] Compare: A. W. Nash, "Torbanite and its Treatment by the Bergius-Method," *J.I.P.T.*, 1926, **12**, 568-581.

the decomposition point of kerogen practically no hydrogenation is taking place ;[9] of the decomposition products or the "products of cracking" of kerogen mainly the lighter products are hydrogenated.

(3) The hydrogenation of the shale prevents the coke-formation.

(4) On hydrogenation, under the same conditions, the shale and the crude shale oil yield oils, of which the lower boiling fractions are almost identical.

(5) The heating of kukersite or its crude oil at temperatures 400–410° C. under 250 kg./sq. cm. hydrogen-pressure favours the formation of oils with lower boiling points, mostly paraffin-, and naphthene-hydrocarbons ; at higher temperatures and on long-continued heating the formation of aromatic hydrocarbons is observed.

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[9] The amount of chlorine giving addition-reaction to the shale is very small as well. See P. N. Kogerman, Sitzungsberichte d. Naturforsch.—Gesellschaft, Tartu, 1927.

The Recovery of Asphaltic Bitumens from Solutions as far as Possible without Altering their Properties.*

By J. Greutert.

The usual methods of separating asphaltic bitumen from solutions result in bitumens being obtained with properties dissimilar to those of the original material, having been considerably altered, partly by the solvent used and partly by the method of reclamation employed. In these methods as much as possible of the solvent is distilled off and the remainder eliminated by thorough stirring on a water bath or at a temperature exceeding the softening point of the asphaltic bitumen by about 100° C. Through this treatment at high temperature, all asphaltic bitumens hardened to a greater or less degree and this hardening was under some circumstances partly counterbalanced by incomplete elimination of the solvent, the result being chance figures. This uncertainty is considered a drawback, particularly in the analysis of sample mixtures of mineral aggregate and asphaltic bitumen taken from road surfaces, for in the majority of cases it is not only desirable to know the percentage of bitumen, but also to be acquainted with its properties in the road surface.

There have been several suggestions in technical literature in recent years for more reliable methods. Prof. Suida[1] distils in vacuo and, moreover, operates in an atmosphere of carbon dioxide, thus making the removal of the major part of the solvent possible at a very low temperature. As, furthermore, only a short period of heating is necessary, this method appears to be suitable for recovering asphaltic bitumen from solutions without considerably changing its properties.

A large number of experiments have been made by this method, and it has been found that the operation of agitating the asphaltic bitumen after distillation under a bell jar with CO_2 can be avoided by removing the last traces of the solvent in the distilling apparatus itself at higher temperature.

Solvent.

It would be of advantage to these distillations if a good solvent for asphaltic bitumen (with a very low boiling point, say, not exceeding 40° C.) were available. Ethyl mercaptan is a solvent of the kind, but, being very expensive and having a very penetrating

* Paper received May 30, 1932.

[1] *Asphalt u. Teer*, 1931, 197.

odour, it is not suitable for general use. It is, however, recommended for scientific work in which operations should be carried out at the lowest possible temperatures. In the present experiments carbon disulphide, chloroform and benzene were at first used. The best results were obtained with carbon disulphide, and for this reason it is preferred, although chloroform and benzene caused only slightly greater hardening. Moreover, carbon disulphide very rapidly dissolves asphaltic bitumen.

Procedure and Equipment.

Fig. 1 shows the construction of the apparatus, the distillation flask being connected to a CO_2 cylinder. An intensive system of condensation is necessary for the condensation of the solvent, and for this two pairs of condensers and receivers are provided and connected in series. If no great importance is attached to the fullest possible recovery of the solvent, one group will suffice. Two tubes (with cocks) are fitted to the receivers so that they can also be emptied during distillation by CO_2 pressure, thus facilitating the uninterrupted distillation of large quantities of solvent. The last condenser is connected to a water-jet pump. A mercury pump can also be connected by means of a three-way cock, but it is not absolutely necessary; it is chiefly used when insufficient vacuum is obtained with the water-jet pump. When the oil bath temperature is above 160° C., however, the mercury pump must in any event be disconnected, as otherwise the oily components of the asphaltic bitumen begin to distil.

Distillation is effected as follows:—

The solution is admitted through the separating funnel into the flask when the oil bath temperature is about 50° C. Then dry CO_2 is introduced, while at the same time the water-jet pump is started. The oil bath temperature is raised to 90° C., at which temperature the solution begins to distil. The CO_2 current is so regulated as to ensure steady and rapid distillation of the solvent, and the temperature of the solution itself is maintained at between 18 and 25° C. When the major part of the solution has distilled, further quantities of solution can, if necessary, be added to the contents of the flask.

Once the largest quantity of solvent has been distilled off in this way, the temperature of the oil bath is increased to about 130° C. (7–10° C. per minute). In the neighbourhood of this temperature some asphaltic bitumens begin to foam, but this can be avoided by quickly increasing the current of CO_2. The oil bath temperature is then raised to about 100° C. above the softening point of the asphaltic bitumen under treatment. So soon as the solvent ceases to distil, cocks A and B are turned off and the current of CO_2

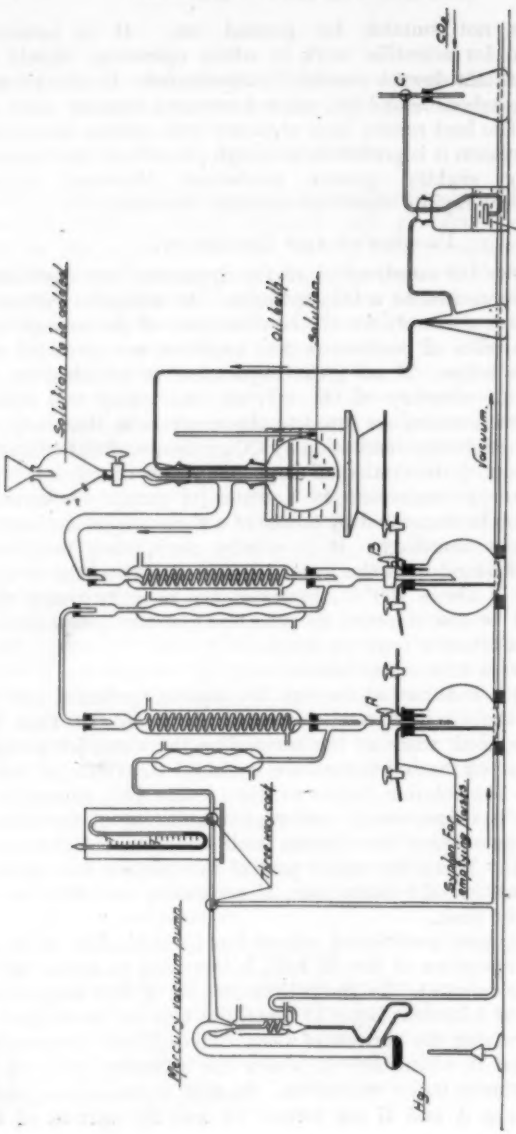

FIG. 1.

CO_2 VACUUM DISTILLATE APPARATUS. FOR THE RECOVERY OF BITUMEN OUT OF SOLUTIONS.

gradually reduced (rapid reduction may cause sudden frothing) until the pressure has dropped to 7–12 mm., this pressure being maintained for about 15 minutes.

After this treatment the asphaltic bitumen is completely separated from the solvent and can be subjected to analysis without further intermediate manipulations. The purity of the bitumen is checked by steam-distilling an asphaltic bitumen treated in the manner described and conducting the escaping vapours through an alcoholic solution of potash. The latter solution has a negative xanthogenate reaction, which proves that all carbon disulphide had been removed from the separated bitumen.

Carried out as above, the distillation of 600 ml. of asphaltic bitumen solution takes about 50 minutes. Even with this improved method certain changes take place, but these are negligible as compared with those which formerly occurred. Thus, the drop in penetration is as follows :—

For asphaltic bitumens with			100	penetration	..	about 4%
,,	,,	,,	above 100	,,	..	4–7%
,,	,,	,,	below 100	,,	..	0–4%

The increase in the Ring and Ball melting point is 0° C. for Spramex, and may amount to 2° C. at the most in the case of harder bitumens.

Finally, it should be noted that the use of moist carbon disulphide generally results in considerable hardening. For this reason dry carbon disulphide was used for all the experiments. This is also an important point in the extraction of asphaltic bitumen from road surfaces. Therefore, prior to the process of extraction, such samples should be thoroughly dried ; if necessary, the solution can be completely dried with anhydrous Na_2SO_4 or $CaCl_2$.

It should be emphasized that bituminous solutions should not stand for longer than 24 hours and the asphaltic bitumen should be reclaimed from them within this period. It has been observed in several instances that, if allowed to stand longer, the properties of the recovered asphaltic bitumen change.

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Petroleum Maatschappij.

The Total Heat and Specific Heat of a Series of Fractions of Petroleum Oil, and Their Relation to Other Properties.*

By H. R. Lang, Ph.D., F.Inst.P., formerly Research Fellow, Institution of Petroleum Technologists, and R. Jessel, B.Sc., A.Inst.P., Demonstrator, Imperial College of Science and Technology.

Part IX.—The Preparation of the Samples of Venezuelan Oil, and the Determination of Some of Their Physical Properties.

By H. R. Lang, Ph.D., F.Inst.P.

1. *Introduction.*—The measurement of certain physical properties of three comparable sets of petroleum oil fractions prepared from Miri, Persian and Venezuelan crude oils was completed in the summer of last year, and the results of the first two have already been published (Parts I.–VIII.),[1] and those for the last set are now given. The comparison of these figures will be found below (Part XII.), together with a general summary and discussion of the results of the whole series of these experiments.

2. *The Preparation of the Samples.*—Five close-cut fractions of 25° C. boiling range were prepared by precisely the same method as had been used previously (Parts I. and VI.)[1], and they may thus be considered to be comparable with the other two sets. As no straight-run kerosine cut was made from this crude, the benzine and gas oil were utilised. Nine batches of the benzine and seven of the gas oil were redistilled in the special one-gallon still, and the average figures obtained were :—

Table I.

Percentages by Volume.

Fraction No. ..	1	2	3	4	5
Boiling range ° C. ..	75–100	100–125	125–150	150–175	175–200
From benzine ..	14·9	19·0	22·6	16·2	13·7
From gas-oil ..	—	—	—	—	6·6

The initial boiling point for the benzine (vapour temperature at the top of the column) was below laboratory temperature, and for the gas oil it was 175° C.. The end point of the benzine was 200° C., and the distillation was therefore stopped at 175° C. and the residue put to Fraction No. 5.

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* Paper received June 27th, 1932.

The samples were kindly supplied by the Asiatic Petroleum Company.

3. *Analysis and Particulars of the Samples.*—The following information was given by Mr. Kewley, to whom grateful thanks are due for much valuable advice :—

(1) Yield of benzine : 14·3 per cent. by weight of the crude.
Yield of gas oil : 11·8 per cent. by weight of the crude.
Yield of fuel oil : 73·9 per cent. by weight of the crude (including water and loss).

(2) Specific gravity :

Benzine, 0·749.	Fuel oil, 0·956.
Gas oil, 0·851.	Crude oil, 0·908.

(3) A.S.T.M. Boiling range :

	Benzine.	Gas oil.	Fuel oil	(Viscosity
I.B.P.	46° C.	208° C.	230° C.	Redwood I at 100° F.
10%	86	228		3260″)
20%	101	238		
30%	112	244		
40%	122	255		
50%	131	266		
60%	140	278		
70%	149	292		
80%	161			
90%	178			
F.B.P.	200			
%—100° C.	19¼%			
%—105	24 %			
%—175		59%		
%—300		77%	7%	

(4) Sulphur Content :

Benzine, 0·06 per cent.	Fuel oil, 1·78 per cent.
Gas oil, 0·53 per cent.	Crude oil, 1·37 per cent.

(5) Wax Content :
Crude oil, 0·31 per cent.
Fuel oil, 0·46 per cent. (melting point 57° C.).

(6) Viscosity of Crude Oil :
Redwood I. at 70° F. 327″.
Redwood I. at 100° F. 149″.

(7) Ash and Water in Crude Oil :
Ash, 0·028 per cent.
Water, 0·2 per cent.

4. *Mean Molecular Weight of the Fractions.*—As in the earlier experiments, the mean molecular weight of each fraction was measured by a cryoscopic method (Parts IV. and VI.),[1] using nitrobenzene as solvent, and a platinum resistance thermometer for the

temperature measurements. The values at zero depression, which have been taken as the correct ones, are given in Table II. The necessary cooling curves were taken with a specially constructed semi-automatic apparatus, and the results for one fraction could be obtained in under an hour. It is suggested that with some such apparatus it may be possible to make this determination a useful standard test.

The relation between specific gravity and molecular weight was not linear for these fractions, but showed a very definite curvature (Fig. 6).

5. *Other Physical Properties*—(*a*) *Boiling Point.*—In Fig. 2 the mean boiling point of these fractions is plotted against the specific gravity and the curve is very nearly linear.

(*b*) *Refractive Index.*—This was measured in precisely the same manner as before, at 20° C., and the results are given in Table II., in terms of the mean wave length of "sodium light"; and its linear relationship to the specific gravity is exhibited in Fig. 2. The value of the empirical specific refraction (Part VI.)[1] is given in the last column of the table for each of these fractions.

(*c*) *Expansion Co-efficients and Specific Gravity.*—The co-efficients of volume expansion were again measured by a weight dilatometer method, between about 6° C. and 50° C., and the results are given in Table II., and are plotted on a specific gravity base in Fig. 4. As before, the values are given in terms of the volume at 15·56° C. (60° F.), and the correction to specific gravity at 60° F./60° F. has also been calculated. The divergence of these results from those given in the Bureau of Standards tables (Circular 154), was nearly the same as for the Persian fractions (Part VI.), namely, the Bureau's figures were 5–9 per cent. lower for oils of corresponding specific gravity, and the divergence increased with decreasing specific gravity.

TABLE II.

Fraction.	Boiling range ° C.	Sp. gr. at 60° F./60° F.	Mean mol. wt.	Refl. index at 20° C.	Coeff. volume expansion per 1° C.	Correction to sp. gr. at 60° F./60° F. per 1° C.	Specific refraction R.
No. 1	75–100	0·7225	87	1·401	0·00128	0·00092	0·5586
No. 2	100–125	0·7437	95	1·413	0·00118	0·00088	0·5587
No. 3	125–150	0·7652	106	1·425	0·00108	0·00083	0·5586
No. 4	150–175	0·7850	121	1·435	0·00101	0·00079	0·5572
No. 5	175–200	0·8092	147	1·448	0·00094	0·00075	0·5564

Part X.—The Temperature Variation Between 0° C. and 100° C. of the Specific Heat of the Venezuelan Fractions.

By R. Jessel, B.Sc., A.Inst.P.

1. *The Results.*—This part of the paper gives the results obtained by the continuous flow electric method on the close cut fractions of 25° C. boiling range, which had been prepared from a Venezuelan crude oil in the manner described above (Part IX.). The apparatus and procedure were identical with those used for the experiments on Miri fractions (Part II.)[1] and on Persian fractions (Part VII.).[1] The results are expressed, as before, in terms of the 20° C. calorie, and the temperatures have been reduced to the gas scale. The specific gravities given are the mean of numerous readings taken during the course of the experiments, and the individual readings agreed very closely among themselves. Especial care was exercised in freeing the samples from dissolved gas, in view of the abnormal results that occur when it is present (Part VII.).[1]

Table III.

Fraction and boiling range.	Specific gravity at 60° F./60° F.	Specific heat cals./gm. ° C.	Temperature ° C.
No. 1. 75° C.–100° C.	0·7225	0·4724	4·1
		0·4898	22·0
		0·5086	39·4
		0·5248	55·1
		0·5331	62·8
		0·5400	69·0
No. 2. 100° C.–125° C.	0·7437	0·4660	4·2
		0·4842	24·5
		0·5060	44·5
		0·5213	61·2
		0·5243	72·9
		0·5490	84·2
		0·5491	85·4
No. 3. 125° C.–150° C.	0·7652	0·4662	12·3
		0·4811	28·8
		0·4945	42·3
		0·5222	70·8
		0·5294	76·5
		0·5374	84·8
		0·5395	85·4
No. 4. 150° C.–175° C.	0·7850	0·4568	4·2
		0·4778	27·7
		0·4944	44·2
		0·5175	68·1
		0·5291	80·6
No. 5. 175° C.–200° C.	0·8092	0·4494	4·6
		0·4676	24·3
		0·4846	43·0
		0·5051	64·5
		0·5227	83·6

These are plotted in Fig. 1.

2. *Discussion of the Results.*—The variation of the specific heat of the fractions from 0° C. up to 100° C. or to the initial boiling point in the case of Fraction No. 1 can best be represented by a series of straight lines. In contradiction to the case of the Miri and the Persian fractions, the temperature co-efficient varies from fraction to fraction, the value increasing with decreasing specific gravity. The equations which best fit the straight lines are :—

Fraction No. 1	.. ..	$s = 0{\cdot}4670 + 0{\cdot}00105t$
,, ,, 2	.. ..	$s = 0{\cdot}4610 + 0{\cdot}00100t$
,, ,, 3	.. ..	$s = 0{\cdot}4540 + 0{\cdot}00097t$
,, ,, 4	.. ..	$s = 0{\cdot}4525 + 0{\cdot}00095t$
,, ,, 5	.. ..	$s = 0{\cdot}4450 + 0{\cdot}00093t.$

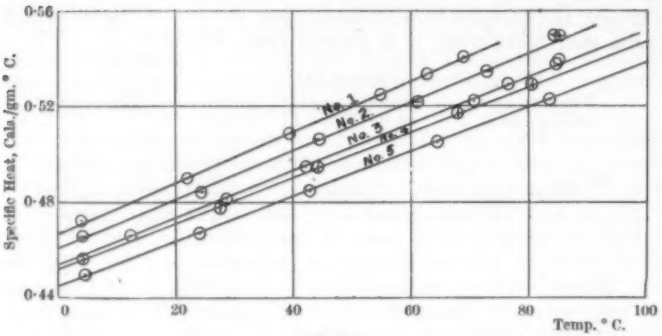


FIG. 1.

In the case of Fractions No. 2 and No. 3 a few points higher than the straight line were obtained, in spite of the care taken to free the oil of air. Although no air was released in the calorimeter, as far as could be seen, it is probable that a small quantity of air remained in solution in the oil, and this would probably account for the abnormal results.

The relation between specific gravity and the specific heat at 30° C. is shown in Fig. 7 as a straight line, but as in the case of the fractions from the other oils a smooth curve may be drawn through the points. It is interesting to note that the portion of this curve in the neighbourhood of specific gravity 0·78 tends to become parallel to the specific gravity axis, just as it does in the case of the Miri and Persian fractions (Parts II. and VII.).[1] The specific heat specific gravity relation is further discussed in Part XII.

Part XI.—Total Heat of the Venezuelan Fractions.

By H. R. Lang, Ph.D., F.Inst.P.

1. *Introduction.*—The total heat of the liquid fractions up to their initial boiling points (vapour temperature) has been measured by the "continuous mixture" method, utilising the apparatus already described in Parts III. and VIII.[1] and elsewhere.[2] In each case the liquids were de-aerated as far as possible in the manner indicated in the earlier papers.

2. *Summary of Observations and Discussion of Results.*—The summarised results are presented in Table IV., and when "runs" had been repeated, only the mean is given. The values in the column headed "Calculated" were obtained from the specific heat curves in precisely the same way as was done for the other sets of fractions (Parts III. and VIII.);[1] the total heat at 0° C. has again been chosen as zero. The results are in terms of the 20° C. calorie. The specific gravity of the samples was checked at frequent intervals and remained in fairly satisfactory agreement with the original figures, showing a change in the fourth place of decimals only.

Table IV.

Fraction Boiling range.	Temperature ° C.	Total heat. Cals./gm. Obs.	Calc.	% diff.
No. 3.				
125°–150° C.	101·21	50·97	50·92	+0·10
	106·74	54·12	53·98	+0·26
	108·28	54·84	54·86	—0·04
	113·17	57·62	57·60	+0·04
	124·03	64·04	63·79	+0·39
No. 4.				
150°–175° C.	102·27	51·27	51·26	+0·02
	119·65	61·00	60·95	+0·08
	136·10	70·78	70·41	+0·52
	149·51	78·40	78·30	+0·13
No. 5.				
175°–200° C.	106·32	52·72	52·58	+0·27
	106·33	52·69	52·58	+0·21
	134·74	68·39	68·40	—0·01
	172·82	91·80	90·80	+1·11
	172·82	91·47	90·80	+0·74

The results once again indicate that the variation of total heat with temperature may well be represented by parabolic equations —*i.e.*, the specific heat-temperature curves may be considered to be linear over this part of the scale.

One of the observations previously noted was that the rapid increase of specific heat in the neighbourhood of the initial boiling point (vapour temperature) appeared to be dependent upon the presence of dissolved air or gas. This, no doubt, is the explanation

of the high results obtained in this region in some of the present experiments, for it is certain that the de-aerator did not by any means completely de-aerate the liquid at these temperatures. It was unfortunate that it was not possible to make further experiments with Fraction No. 5 at the highest temperature, which is only just over 3° C. below the initial boiling point. Each of the values obtained are much higher than could be accounted for by experimental error. It is to be noted here that the second set of experiments at about 106° C. with this fraction—performed some days after the first set—reproduced the earlier result with remarkable precision.

In Table V. the total heat of the five fractions is given from 0° C. up to their initial boiling point (vapour temperature), and the method of calculation and mode of use of the table has already been given (Parts V. and VIII.).[1]

TABLE V.

Temperature.	Total heat. Cals./gm. Fraction.				
° C.	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
0	0·00	0·00	0·00	0·00	0·00
10	4·72	4·66	4·59	4·57	4·50
20	9·55	9·42	9·27	9·24	9·09
30	14·48	14·28	14·06	14·00	13·77
40	19·52	19·24	18·94	18·86	18·54
50	24·66	24·30	23·91	23·81	23·41
60	29·91	29·46	28·99	28·86	28·37
70	35·26	34·72	34·16	34·00	33·43
80		40·08	39·42	39·24	38·58
90		45·54	44·79	44·57	43·82
100		51·10	50·25	50·00	49·15
110			55·81	55·52	54·58
120			61·46	61·14	60·10
130				66·85	65·71
140				72·66	71·41
150				78·56	77·21
160					83·10
170					89·09

PART XII.—SUMMARY AND GENERAL DISCUSSION OF THE RESULTS.

By H. R. LANG, Ph.D., F.Inst.P., and R. JESSEL, B.Sc., A.Inst.P.

1. *Introduction.*—With the completion of the measurements made on the third set of fractions (prepared from a Venezuelan crude) a further step in the research has been made, and this occasion is convenient to summarise and discuss the results so far obtained.

The aim of the work has been to investigate the possibility of representing the thermal changes which take place during refinery processes by one or more simple equations. Several such equations have been proposed from time to time by various workers in this

field, but it appears that no single universal equation can be found to represent any one property of all types of oil. The question that then arises is, whether it is possible to find a sufficiently approximate formula in which the constants are made to vary according to the type of oil under consideration. It is also desirable to be able to express any property which is less easy of direct measurement in terms of one which can be readily measured; for example, specific heat is sometimes expressed in terms of specific gravity.

It has been the practice in the past to express as many properties as possible in terms of the specific gravity, but recent work has shown that this quantity is not as good an "index figure" to the other properties of a petroleum oil as had been supposed. It is suggested that a function of the specific gravity, together with the refractive index of the specimen, may subsequently prove a valuable "index figure," although at present the insufficiency of reliable data, especially as regards the heavier fractions, renders it impossible to make a thorough test of this proposal.

The problem which we set ourselves was set out in an earlier paper,[3] and was further elaborated in Part I. of this series.[1] Specially prepared close-cut fractions have been systematically examined, and in addition the specific heats of some crude oils before and after topping have been measured. Twenty-four samples in all have been tested. Five fractions from each of three crude oils were prepared in such a way (Part I.)[1] that they could be considered comparable. They were of 25° C. boiling range, and the initial points (vapour temperature) were: 75° C., 100° C., 125° C., 150° C. and 175° C.

The three crudes from which the fractions originated were:—

Miri	Naphthene base,
Persian	Mixed base,
Venezuelan	Asphalt base,

and the detailed results for each set has been given in Parts I.–V., VI.–VIII.[1] and IX.–XI. (above) respectively.

It remains now to summarise and compare the three sets with each other, and with the earlier results obtained with some crudes and topped crudes. Following the earlier practice, this is done on a specific gravity basis.

2. *Discussion of Results.*—(*a*) *Boiling Point.*—The plots of the mean boiling point against specific gravity are collected for comparison, in Fig. 2. Corresponding Persian and Venezuelan fractions have almost the same specific gravity, while in each case the corresponding Miri fraction has a specific gravity about 3 per cent.

higher. The rate of change of specific gravity with boiling point is roughly the same in all three cases.

(*b*) *Refractive Index.*—The relation between the refractive index and the specific gravity was in all three sets a linear one (Fig. 2); but the empirical specific refraction, R, appears to be a characteristic constant for each set of samples studied, and it is this quantity,

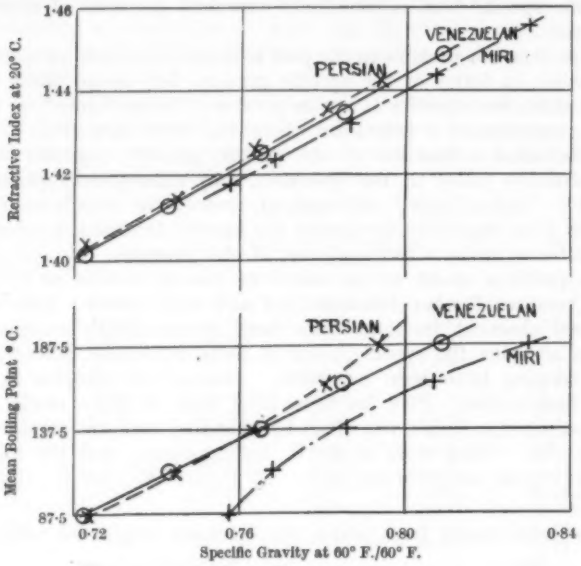


FIG. 2.

or some similar quantity, that may prove to be a valuable "index figure" to other properties. The value of R is defined by the equation :—

$$R = (n_{20}-1)/d_{20}$$ where n_{20} = refractive index at 20° C.
d_{20} = density at 20° C.

Gladstone and Dale's well-known empirical law states that for any one substance R is very nearly independent of temperature, and is almost the same whether the substance is in liquid or gaseous form. Various similar functions have been proposed, and some of these expressions have been derived from theoretical considerations, but for the present purpose the quantity R, as defined above, gives as consistent results as any, and has the advantage of being the

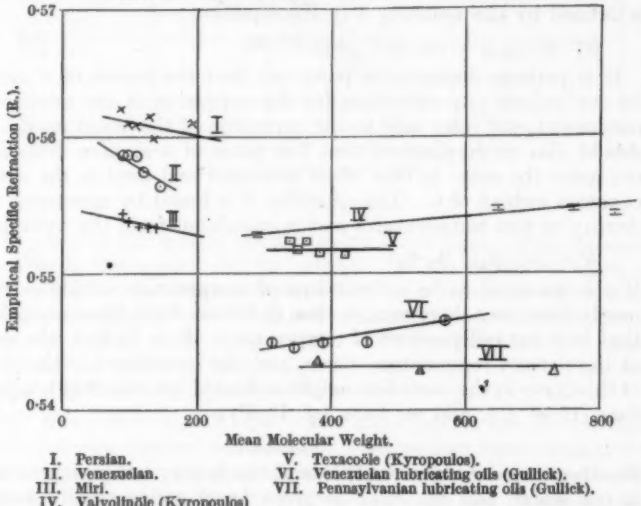
simplest. In the table the values for the three sets of fractions are set out, and it will be observed that the difference between the means is sufficiently greater than the deviation of any one value from the mean of that set (given in Table VI.) to enable this test to decide to which set the specimen belonged.

TABLE VI.

Empirical specific refraction (R).

Miri.		Persian.		Venezuelan.	
R	Dvn $\times 10^4$	R	Dvn $\times 10^4$	R	Dvn $\times 10^4$
0·5546	+8	0·5618	+ 9	0·5586	+ 7
0·5539	+1	0·5608	— 1	0·5587	+ 8
0·5536	—2	0·5608	— 1	0·5586	+ 7
0·5536	—2	0·5615	+ 6	0·5572	— 7
0·5535	—3	0·5598	—11	0·5564	—15
Mean .. 0·5538		0·5609		0·5579	
Difference		0·0071		0·0030	

This interesting result was pursued a little farther, and the observations of Gullick[4] and Kyropoulos[5] were used. The values are exhibited graphically in Fig. 3. So far as the present work



I. Persian.
II. Venezuelan.
III. Miri.
IV. Valvolinöle (Kyropoulos)
V. Texacoöle (Kyropoulos).
VI. Venezuelan lubricating oils (Gullick).
VII. Pennsylvanian lubricating oils (Gullick).

FIG. 3.

has gone, it does not appear that the value of R is dependent upon the " base " of the sample, nor does it appear to be a characteristic constant of any given homologous series. In fact, some such

assumption was made by Kyropoulos in an attempt to analyse lubricating oils, but his results are not at all convincing, and they have been criticised by Beilenberg.[6]

(*c*) *Expansion Co-efficients.*—The thermal expansion determinations were carried out, in the first place, only for the purpose of making the small corrections necessary to reduce the specific gravities measured to a standard temperature (15·56° C.); but the results obtained diverged sufficiently from the accepted figures for petroleum oils of corresponding specific gravity that it was considered desirable to carry out a series of rather more careful measurements. It is claimed that the present results are accurate to 1 per cent., and they are expressed in terms of the volume at 15·56° C. In order to avoid any uncertainty the quantities are are here defined again.

The co-efficient of volume expansion is the quantity a in the equation :—

$$V_t = V_{15\cdot56}\,[1 + a\,(t-15\cdot56)] \quad .. \quad .. \quad .. \quad .. \quad (1)$$

where V_t is the volume at t° C.

And the correction to specific gravity at 15·56° C./15·56° C. is defined by the quantity b in the equation :—

$$(\text{sp. gr.})_{15\cdot56} = (\text{sp. gr.})_t - b\,(t-15\cdot56) \quad .. \quad .. \quad (2)$$

It is perhaps desirable to point out that the values of a and b do not include any correction for the expansion of the measuring instrument, but refer only to the expansion of the liquid itself. It should also be emphasised that the value of b as here defined is not quite the same as that often measured and used in the above equation instead of b. This quantity b^1 is found by measuring the density at two temperatures and is calculated from the formula :

$$b^1 = (d_1-d_2) / (t_1-t_2) \quad .. \quad .. \quad .. \quad .. \quad (3)$$

If a is assumed to be independent of temperature, which is very nearly true over short ranges, then it follows from these equations that b^1 is not independent of temperature. It is, in fact, the slope of the density-temperature curve, and the quantity b is the slope of this curve in the *immediate neighbourhood* of the standard temperature (15·56° C.), and we have (*cf.* Duff[7]) :—

$$b = -d_{15\cdot56}\,(a).$$

In other words, if equation (1) is true, the density-temperature curve is not linear, and the slope as given by b^1 will naturally depend upon the particular two points that are chosen to obtain it.

In Fig. 4 the co-efficients of volume expansion a of the special fractions and of two other heavier samples are compared graphically on a specific gravity base. The values derived from the Bureau of

Standards tables (Circular 154) are also shown, and as has been indicated in the earlier parts of these papers, the present figures are consistently higher than those given in these tables. Recently, however, Cragoe and Hill[3] have published a further paper on the subject in which they state: "There appears to be no simple relation between thermal expansion and gravity which will be adequately representative of present-day motor fuels, including both straight-run and cracked gasolines and also benzol blends. Thus, the accuracy with which the data in Circular No. 154 are applicable to motor fuels in general appears to be rather limited."

So far as the likely composition of the present samples is known, our results are consistent with the published data for the expansion of the various hydrocarbon series of compounds.

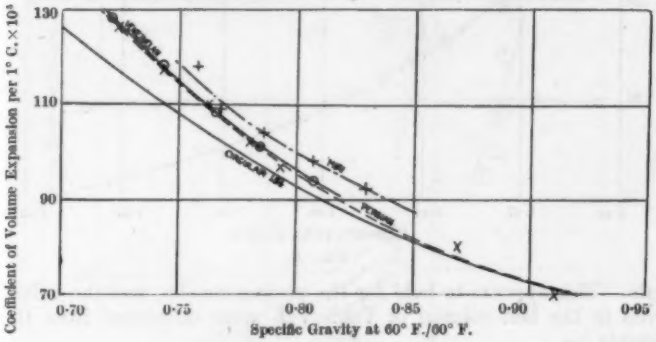


FIG. 4.

In place of the specific gravity as an index figure of the thermal expansion, the present results indicate that the refractive index is fairly satisfactory. The results plotted on a refractive index base are shown in Fig. 5, from which it is seen that the greatest divergence from the smooth curve is 3 per cent. It is possible that here again the most satisfactory "index figure" may prove to be a function containing both the refractive index and the specific gravity.

(*d*) *Mean Molecular Weight.*—The investigation has shown that the cryoscopic method can be made a simple and rapid method for the determination of the mean molecular weight of petroleum oils, especially if some automatic method is used for obtaining the necessary cooling curves. The details of the technique developed have been given by Steed (Part IV.),[1] Gullick[4] and Lang (Part VI.),[1] and it has been shown that, provided that depressions of not more than three or four degrees Centigrade are used, the figures obtained

for the mean molecular weight are a linear function of the depression. This enables an extrapolation to zero depression to be carried out, and it is this value that is taken as the correct one. It does not now seem a very large step for the determination of mean molecular weight to become a routine laboratory test.

A good approximation can be obtained for the mean molecular weight, at any rate for the lighter fractions, from the mean boiling point. It is well known that in any homologous series the molecular weight bears a simple relation to the boiling point on the absolute

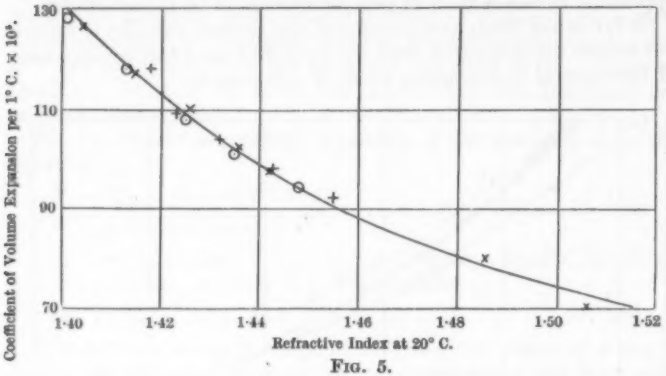


FIG. 5.

scale. This appears to hold for the present results, and the values given in the last column of Table VII. were calculated from the formula :—

$$M = (T/39)^2$$ where M = mean molecular weight.
T = mean boiling point on the absolute temperature scale.

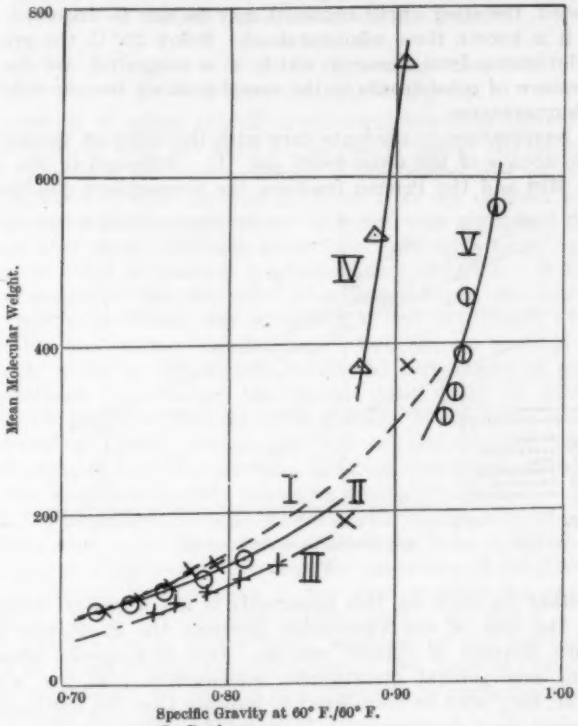
TABLE VII.

Fraction No.	Mean boiling point.	Mean molecular weight. Miri.	Persian.	Venezuelan.	Calculated.
1	87·5° C.	88	85	87	85
2	112·5	97	100	95	98
3	137·5	108·5	114	106	111
4	162·5	125	126	121	125
5	187·5	140	135	147	140

In Fig. 6 the mean molecular weight is plotted on a specific gravity base, and some values that had been obtained for heavier fractions by Gullick[4] and others using the same technique have been included. These suffice to show that the linear relationship previously noted was only an approximation over the short range then considered. The results also show that the mean molecular weight cannot be expressed in terms of the specific gravity only,

that is that here again the specific gravity is not a suitable index figure.

(*e*) *Specific Heat and Total Heat.*—Perhaps the most interesting point that arises from both the specific heat and the total heat



I. Persian.
II. Venezuelan.
III. Miri.
IV. Pennsylvanian lubricating oils (Gullick).
V. Venezuelan lubricating oils (Gullick).

FIG. 6.

measurements is that, if consistent and exactly reproducable results are to be obtained, especially in the neighbourhood of the initial boiling point, the oils must be free from dissolved gases. Our experiments have repeatedly shown that, when dissolved gas is present, results higher than the normal values are obtained; the peculiar shape of some of the specific heat-temperature curves must be attributed to this cause.

The experiments by both methods show that, except for two of the crude oils (Pennsylvanian and Persian), the variation of specific heat with temperature is almost linear from about 25° C. right up to the initial boiling point. In the case of the two oils mentioned, the steep curve obtained may be due to dissolved gas which it is known these oils contained. Below 25° C. the graphs show deviations from linearity which, it is suggested, are due to the presence of constituents in the samples which become solid at these temperatures.

The temperature co-efficients vary with the different specimens, but are always of the order 0·001 per ° C. Although in the case of the Miri and the Persian fractions the temperature co-efficient

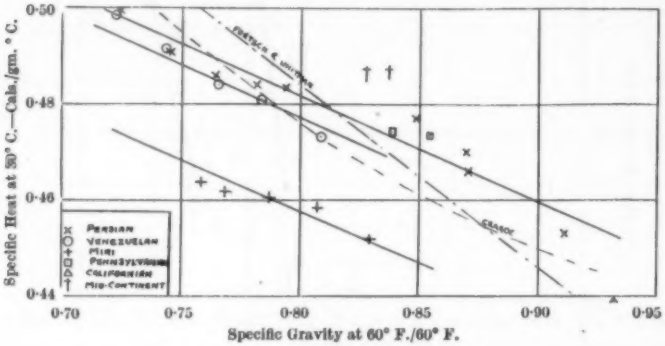


FIG. 7.

is constant for each oil, this apparently is not a general relation, for in the case of the Venezuelan fractions the co-efficient falls off with increase of specific gravity. Our own results scarcely warrant any general quantitative relationship. On the whole, however, they may be considered to indicate that the temperature co-efficient does decrease with increase of specific gravity.

In the earlier parts of this series of papers, smooth curves have been drawn to show the relation of specific heat to specific gravity for each set of samples. Our results are collected for comparison in Fig. 7. The curves derived from the equations of Fortsch and Whitman[9] and of Cragoe[10] are also shown. The specific heat at 30° C. has been chosen, but since the temperature co-efficients are all of the same order, the relative positions of the points will be but little changed had some other temperature been chosen. To an approximation sufficiently accurate for most practical purposes, the results show that the specific heat-specific gravity relation is linear for each set of samples originating from the same crude.

That is, in general, the specific heat at any one temperature may be represented for petroleum oils of the same origin by an equation of the form :—

$$s_t = a - bd$$

where s_t is the specific heat at $t°$ C.,
a is a constant,
b is the slope of the line,
and d is the specific gravity.

The results of others as well as our own show that the value of b is sufficiently near the same for all oils to justify the adoption of one value for it, for the convenience of the technologist who requires an equation of wide application, rather than one of great accuracy with only a limited application. All observers are agreed that the value of a varies, although some have adopted a mean value for this, in order to produce a general linear equation. It has also been suggested that the value of a depends upon the base of the oil, and, even if this view is correct, it will be difficult to obtain suitable quantitative relationships. Further, an analysis of the sample would be required to decide the percentages of paraffins, naphthenes, etc., before the specific heat could be calculated. It is now suggested that the value of a may be connected with some function of the specific gravity and refractive index, and it is interesting to note that its value is roughly proportional to that of R, the empirical specific refraction discussed above.

3. *Acknowledgments.*—We welcome this opportunity of acknowledging once more the great assistance we have received during the course of the work. Through the generosity of the Institution of Petroleum Technologists it has been possible for one of us (H.R.L.) to devote two years to the work. We desire to record our grateful thanks to the many members of this Institution as well as to our friends and colleagues at the Imperial College, who have so willingly encouraged and helped us to surmount the many difficulties with which we have met.

References.

[1] Parts I.–V. of these papers, *J. Inst. Petr. Techn.*, 1930, **16**, 783–813; Parts VI.–VIII. of these papers, *J. Inst. Petr. Techn.*, 1931, **17**, 572–584.
[2] Lang, *Proc. Phys. Soc.*, 1931, **43**, 572.
[3] Lang and Jessel, *J. Inst. Petr. Techn.*, 1930, **16**, 476.
[4] Gullick, *J. Inst. Petr. Techn.*, 1931, **17**, 541.
[5] Kyropoulos, *Zeits. f. phys. chem.*, 1929, **144**, 30.
[6] Beilenberg, *Zeits. f. phys. chem.*, 1930, **149**, 42, and 1931, **154**.
[7] Duff, *J. Inst. Petr. Techn.*, 1930, **16**, 501.
[8] Cragoe and Hill, *Bur. Standards J. of Research*, 1931, **7**, 1133.
[9] Fortsch and Whitman, *Ind. Eng. Chem.*, 1926, **18**, 795.
[10] Cragoe, *Misc. Publications, Bur. Standards, No.* 97, 1929.

Experience with "C.I." Engines in L.G.O.C. Service.*

By A. A. M. Durrant.

Engines.

Junkers.—Following an examination of several "C.I." engines, the first actual experience with the type was obtained in February, 1929, when three Junkers type S.A.9. engines were purchased.

It was originally hoped to fit these engines to an omnibus, but owing to the unusual shape and high torque at low speeds this was not rendered possible; they were, therefore, fitted to two A.E.C. "5" type lorries.

The characteristics and performance of this engine and the vehicles to which they are fitted, together with the other engines described herein, are given in Table I.

The construction of this engine is well known and results in the following advantages:—

1. High specific output (15 h.-p./litre: compare later engines);
2. Good mechanical balance;
3. Gas and inertia loads balanced within the crankshaft and connecting rod assembly, and no load carried by the main bearings.

These engines were very reliable, the only real trouble experienced being a rather heavy loss in power in one case. At this time it was very usual to refer to these engines as "crude oil" engines—would run on anything. Actually we used a gas oil with every intention of substituting the cheaper Diesel oil, when sufficient data had been obtained. The loss in power mentioned was traced to slight scoring of one fuel pump, caused by the presence in the gas oil of suspended particles sufficiently small to pass the inadequate fuel filter fitted. It will be appreciated that under the high injection pressure employed on this engine (10,000 lb./sq. in.) a few scratches on the plunger are sufficient to cause loss of pressure and leakage of fuel. Experience taught us that it was essential to use as clean a fuel as possible for the "C.I." engine and, at the same time, provide an efficient filter, and no trouble of this kind has since been encountered with the various engines which we have had in service. It is, nevertheless, up to the oil companies fully to appreciate the requirements of the "C.I." engine, which are for a fuel as free from dirt and water as is petrol.

* Paper read before Oil Industries Club on April 5, 1932.

The lubricating oil used was a relatively high grade material of viscosity of about 220 seconds at 140° F.; somewhat heavy dilution was experienced.

A.E.C. High Speed Oil Engines.—(1) *Acro Type.*—First actual service experiments were commenced in January, 1931, when three "ST" type four-wheeler omnibuses, fitted with A.E.C.-Acro High Speed Oil Engines, were operated. In March the experiments were extended by the addition of nine "LT" type six-wheeler omnibuses.

The engine operated on the Acro principle, the air cell being located in the cylinder head. It might be pointed out that the success of the Acro system depends on the very delicate balance of several factors, the most important of these being the shape and size of the venturi, injection characteristics and compression ratio. The performance of the engine was then far in advance of any of its contemporaries, its most important valuable feature probably being its wide speed range, which was at least 50 per cent. greater than any other engine existing at that time. The actual operation of the engine in the omnibus was satisfactory. At idling the "Diesel Knock" was apparent, though when a road speed of about 10 m.p.h. was attained, it was practically impossible to distinguish between this engine and a petrol engine.

Although the operation of these twelve vehicles was treated experimentally by this company, they were performing regular service schedules. The object of this full scale experiment was to enable development work to proceed rapidly by having the advantage of service experience.

Prior to commencing service experiments with "C.I." engined vehicles, it was thought that accidental and unavoidable spillage of a rather pungent smelling fuel on to the body of the vehicle, and its seepage to the interior in the vicinity of the fuel tank, would constitute a serious and perhaps fatal objection. This was soon proved to be quite unfounded, and most careful observations for a period of a year have failed to detect any marked odour of fuel even where an oily patch is visible inside the vehicle. When the vehicles were first put into service, complaints from the general public regarding odour of exhaust fumes were not infrequent; how much of this was due to really obnoxious fumes was difficult to say. With regard to smoke, when operating under heavy injection this was noticeable.

As the result of this early experience with the Acro system, the A.E.C. developed a new type of engine in conjunction with Mr. Ricardo, this being described later on. Service tests with the first of these new engines showed such marked advantages,

that it was decided to convert the existing twelve Acro engines to this later type. At the time of this conversion (October, 1931) an order for a further twenty Renown chassis, fitted with the A.E.C. Ricardo engine, was being executed.

(2) *Ricardo Type.*—As already mentioned the A.E.C. evolved a new type of engine, the basis of the design being Mr. Ricardo's principle of "Rotational Air Swirl." In this system the air, due to the orderly turbulence imparted to it, searches out the fuel rather than the fuel searching out the air. This method enabled a larger amount of the available oxygen to be utilised than occurred with the Acro engines, and hence the specific output and consumption of the engine have been improved. The combustion process is very much more efficient, and an absolutely smokeless exhaust is obtained under all operating conditions: the only time when smoke is apparent is on acceleration, when a slight momentary puff is emitted. The smoothness and general running of the engine have also been improved, in addition to economy. It is a significant fact that since the conversion to the new type of engine, not a single complaint regarding smell or smoke has been received from any quarter, though a greater aggregate mileage than that performed by the Acro type has already been operated. During the earlier part of their time in service the fuel used for these engines was of a distinctly pungent character, and our experience would appear to indicate, therefore, that where combustion is satisfactory exhaust odour is largely independent of fuel odour. The oil companies, however, should not relax efforts to reduce fuel odour to a minimum since the public taste will eventually become as discriminating to "C.I." engine fuel as it is at present to petrol.

The service results obtained with the A.E.C. engines are given in Table I., but are briefly summarised here in regard to the "L.T." vehicles:—

A.E.C. Acro. Mileage, 251,000.

A.E.C. Ricardo. Mileage, 324,000.

Consumption of Ricardo type as percentage of Acro, 92 per cent.

Consumption of Ricardo type as percentage of petrol engines, 63 per cent.

The figures shown are, of course, based on actual consumption and not m.p.g. values; the saving in fuel cost is considerably greater owing to the absence of tax on gas oil. It will be seen, however, that even should this fuel become taxed, the "C.I." engine will still show a substantial and attractive economy in fuel as compared with the petrol engine.

Gardner Type 5 L.W.—An experimental "L.T." six-wheeler omnibus has just been placed in service fitted with one of the new Gardner engines. Limitation of space only allowed a five cylinder unit to be installed, particulars of which are given in Table I. With regard to B.M.E.P. the performance of this engine is strictly comparable with a petrol engine, but owing to the limited speed of 1700 r.p.m. the specific output and weight per h.-p. do not show to advantage.

The engine operates with an open combustion chamber on the principle of Directed Fuel Spray. This method is the converse of the Ricardo type, insomuch as the fuel has to search out the air by the aiming of several fine sprays, together with rather indiscriminate turbulence. The rotational speed of the engine is limited to a certain extent by the time taken for the fuel to traverse the combustion chamber. The advantages of the system lie in a compact combustion chamber, so that heat losses during compression and combustion are low, thus resulting in a high efficiency and the engine being an "easy starter." The success of the Gardner engine lies largely in the excellence of its spraying mechanism.

The engine has not been in service long enough to allow definite fuel consumption figures to be given. There is indication, however, that the figure will be a very satisfactory one, though any possible advantage in this direction is much offset by the fact that the vehicle, when geared to give the same accelerating performance as that of our other vehicles, has a maximum speed of only 25 m.p.h.

The experience of the L.G.O.C. with compression ignition engined vehicles which they have been operating experimentally has satisfied their engineers that there is a definite future for the high speed compression ignition engine for omnibus operation. This is based upon the confirmation of the following advantages which this type of engine possesses as compared with the petrol engine:—

1. The "C.I." cycle definitely introduces higher specific economy, so that even were the cost of the "C.I." fuels, together with any tax which might ultimately be applied, reach the same level as that of petrol, an appreciable saving in fuel costs would still be attainable, and it is reasonable to assume that the cost of this fuel would not rise above that of petrol.
2. The safety factor—*i.e.*, immunity from fire risk both on the road and in the garages. Whereas the feature of safety on the road is clearly of great importance, the advantage of using a non-volatile fuel in the garages is also of considerable advantage for the reason that the many restrictions at present imposed in respect of the storage of petrol would, without

doubt, be removed. For example, the authorities would no doubt waive the present regulation in respect of providing open areas at fuelling points, etc., so that greater advantage could be taken of the garage site.

3. Manœuvrability. The enhanced accelerating capabilities of the "C.I." engines and their well-sustained torque facilitate driving in congested areas.
4. It is unnecessary to allow protracted time for warming up when starting from cold in the garages, thus saving time and also reducing the fumes, etc., which collect in the garage when a large number of vehicles is being started up preparatory to leaving for the road.
5. The exhaust from the "C.I." engine, although possessing a distinctive odour, is innocuous on account of the reduced amount of carbon monoxide produced during combustion.

Fuel and Lubricants.

Fuel.—As already mentioned, commercial gas oil was used for the Junkers engines and was also employed for the A.E.C. Acro engines, whilst a Diesel oil was in use when these engines were modified by fitment of the Ricardo head. Performance was not all that could be desired, but there was no guidance as to a suitable alternative. A research was, therefore, commenced in conjunction with the A.E.C., and a large variety of fuels was tested. It was soon learnt that any fuel would not do, and that only a relatively small proportion of those available gave satisfactorily smooth running. This fact also became realised by the oil companies, and their independent researches led to development of fuels designed for the high speed engine, as against the previous policy of offering a material of suitable viscosity but otherwise bearing no relation to the requirements of the engine. To-day it is appreciated by all that a "C.I." engine fuel requires as much care in its selection as does one for a petrol engine. It also seems to be established that the only sure test of a fuel is its performance in an engine. Our researches included a most detailed examination of the various fuels in the laboratory, but apart from ignition temperature no test was sufficiently related to performance to be of any value apart from checking consistency of supply—even ignition temperature fails in certain instances. As a result of this work, the fuel now being used is proving much more satisfactory than those originally employed. We have certainly not reached a stage where a firm specification can be given; the tentative specification given in Table II. was, however, prepared to serve as a rough guidance to those using the A.E.C. engine.

As a side line in the fuel research referred to, laboratory and where possible engine tests were made with fuels derived from coal. The results were in every case most disappointing, and it would almost seem that the best means of utilising our home produced fuel would be on the lines of designing an engine specially adapted to it. Experiments were also carried out with doped fuels, ethyl nitrate being used. Whilst this substance will facilitate the combustion of an indifferent fuel, its effect on a satisfactory fuel is not marked and its use is a question of economics.

Lubricant.—The lubrication of the "C.I." engine is a problem which is still under investigation, and the specification given in Table III. merely indicates the type of oil we have up to now used in the A.E.C. engines.

A more viscous and, from some points of view, higher grade oil was used for the Junkers engines, whilst a more viscous oil has also to be used for the Gardner type. Both these types of engine, but particularly the latter, exhibit very heavy crankcase oil dilution.

The A.E.C. engine is exceptional in that dilution is very low, the crankcase oil only containing about 2 per cent. of fuel. This means that instead of getting progressively thinner as in the case of other types of engine, the oil thickens during use due to the accumulation of suspended matter. The problem of lubrication of this engine differs from that of a petrol engine in that: (1) dilution is much less, and (2) the carbon which accumulates is very finely divided and does not settle out to form a sludge. It has been considered desirable, therefore, to employ an oil of relatively low viscosity (150–170 secs. at 140° F.), and whilst tests have been planned with various different types of oil, this one essential feature of low viscosity is being retained. The amount of suspended matter increases steadily with mileage at a rate of something like 1 per cent. per 1000 miles run. Whilst it is realised that, under the conditions operating in the cylinder of a "C.I." engine, oil is likely to become oxidised more rapidly than an oil in a petrol engine, a certain, but at present undetermined, proportion of the suspended carbon is probably the result of incomplete combustion of the fuel. There is evidence for stating that the amount of carbon in the used oil has decreased since the substitution of the Ricardo head for the Acro type.

We are often told that only the most expensive grades of oil are suitable for "C.I." engines. It will be appreciated, however, that we are not anxious to offset our saving in fuel costs by a large increase in our lubricants bill, and the oil companies should bear this in mind when making recommendations.

It would be very unwise for the suppliers of lubricating oils to be dogmatic in regard to the type of lubricant best suited for use with compression ignition engines. Experience has shown that two entirely different characteristics are exhibited in two different makes of engine, both of which could be regarded as operating efficiently, so that it would be well for those concerned to study carefully the requirements of each individual make of engine, at any rate at our present stage of knowledge, before making definite recommendations to operators.

TABLE I.

SUMMARY OF CHARACTERISTICS AND PERFORMANCE OF C.I. ENGINED VEHICLES IN L.G.O.C. SERVICE.

	Junkers S.A.9.	A.E.C. Acro.		A.E.C. Ricardo.	Gardner 5.LW.
No. of cylinders ..	2	6		6	5
Bore X Stroke m/m ..	80×300	110×142		115×142	108×152.4
Swept Volume, litres..	3.003	8.10		8.86	6.975
Mode of Operation ..	2-cycle Direct Injection.	4-cycle Acro Air Cell.		4-cycle Rotational Air Swirl.	4-cycle Directed Fuel Spray.
B.H.P. and Speed ..	45@1100	95@2500		130@2400	85@1700
Max. B.M.E.P., lbs. per sq. in.	94	83		103	102.5
B.H.P. per litre ..	15	11.7		14.7	12.20
Wgt. with Electrical Equipment, lbs. ..	969	1350		1415	1467
Ditto., per B.H.P. lbs.	21·5	14.2		10.9	17.0
Type of vehicle to which fitted ..	A.E.C.-5 type Lorry.	3 to ST. 4-wheel Bus.	9 to LT. 6-wheel Bus.	LT. 6-wheeler.	LT. 6-wheel Bus.
Aggregate Mileage ..	26,200	112,800	251,200	324,800	—
Grand Total Mileage..	—	—	688,800	—	—

TABLE II.

TENTATIVE SPECIFICATION FOR FUEL FOR A.E. CO. HEAVY OIL ENGINE.

Description	The fuel to be a hydrocarbon oil of petroleum and/or shale origin. To be free from mineral acid, grit and other foreign impurities of all descriptions.
Closed Flash Point ..	Not to be below 150° F.
Viscosity	Measured on the Redwood No. 1 Instrument, at 100° F., not to exceed 45 sec.
Cold Test	The Pour Point of the oil not to be above 20° F. Method of test: A.S.T.M. Serial Designation D.97.22.T. (See also I.P.T. Standard Methods of Testing, First Edition, G.O.11, page 38.) No crystalline or other deposit to form during the test above or at the specified Pour Point.
	Note.—This Cold Test should meet the requirements of an oil for winter conditions in Great Britain. The test may be excluded or made more stringent, as considered desirable, if the oil is used in other countries.

TABLE II.—*continued.*

Water	Nil.
Adventitious Matter ..	Not to exceed 0.03%.
Ash Content (Inherent)	Not to exceed 0.01%.
Sulphur Content ..	Not to exceed 0.05%.
Spontaneous Ignition Temperature.	Depends on type of apparatus used for test. Temperature should, however, be as low as possible.
Performance	The fuel must give satisfactorily smooth running when tested in the engine.

TABLE III.

TENTATIVE SPECIFICATION FOR ENGINE LUBRICATING OIL FOR A.E. Co. HEAVY OIL ENGINE.

Description	To be a pure hydrocarbon oil, thoroughly filtered to remove all solid matter, and to be entirely free from water, fluff or any other impurities. The cylinder oil used in its composition to be of the filtered variety. The oil to possess a neutral reaction.
Specific Gravity ..	Measured at 60° F., not to be above 0.930.
Closed Flash Point ..	Measured on a Pensky Marten's or Gray's apparatus, not to be below 360° F.
Viscosity	Measured on Redwood's standard instrument, not to exceed 1800 sec. at 70° F., not to be below 150 sec., nor to exceed 170 sec. at 140° F., and on no account to fall below 55 sec. at 200° F.
Asphalt	Not to exceed 0.005%.
Ash	Not to exceed 0.010%.
Cold Test	The Pour Point of the oil as determined by the I.P.T. method, G.O.11 (A.S.T.M. Serial Designation—D.97—22. T.), not to exceed 15° F.
Colour	Determined in a Lovibond Tintometer, using a $\frac{1}{4}$-in. cell and standard glasses, Brown Series No. 500, not to be deeper than 250.

Progress Report of International Studies on Nomenclature and Properties of Motor Fuels.

By American National Committee, World Power Conference.

At the Annual Meeting of the International Executive Council of the World Power Conference, in London in 1931, the American National Committee submitted a report upon what had been done in the United States on the matters covered by Fuel Conference resolutions :—

A.—Properties of Coal,
B.—Calorific Value of Fuels,
C.—Powdered Fuels, and
D.—Motor Fuels.

In the discussion upon Resolution D it was proposed and agreed that the American National Committee be requested to use its influence to bring about, through American standardising agencies, international action on Resolution D as well as on proposals advanced by the German National Committee for international standardisation of the nomenclature of liquid fuels. In response to this request the American Committee submits the following report.

The International Federation of National Standardisating Associations (I.S.A.) was formally established in 1929. It is understood that at the present time there are represented in the I.S.A. the standardisation associations of the following eighteen countries :—

Austria.	Germany.	Poland.
Belgium.	Holland.	Rumania.
Czechoslovakia.	Hungary.	Sweden.
Denmark.	Italy.	Switzerland.
Finland.	Japan.	United States.
France.	Norway.	U.S.S.R.

In the same year in which the I.S.A. was organised, 1929, the standardising body of the U.S.S.R. suggested to the I.S.A. that international co-operation on standardisation of petroleum products be undertaken. The I.S.A. canvassed its member bodies on the proposal. The American Standards Association (A.S.A.) called into conference the American Society of Testing Materials (A.S.T.M.), the American Petroleum Institute, the U.S. Bureau of Standards and several of the major oil companies. As a result of inquiries thus made the American group was of the opinion that while it was too early to undertake international standardisation of quality

specifications, international unification of nomenclature and of methods of testing would be of great value, and that such unification should precede the preparation of specifications. It so reported to the I.S.A.

At the meeting of the I.S.A. in Paris in May, 1930, the American proposals were adopted, a technical committee, No. 28, on petroleum products was created, and the A.S.A. was requested to assume the secretariat. The A.S.A. thereupon placed the technical end of this work in the hands of a sectional committee having the same membership as the Committee D-2 on Petroleum Products and Lubricants of the American Society of Testing Materials. Dr. R. P. Anderson, Secretary of the Division of Refining of the American Petroleum Institute and Secretary of the Sectional Committee, was appointed A.S.A. representative on the I.S.A. Technical Committee No. 28.

In pursuance of its secretariat duties, the A.S.A. addressed a letter to the member bodies of the I.S.A. calling attention to the formation of the Technical Committee, enclosed with this letter a memorandum explaining the organisation of standardisation procedure in the United States, and suggested that each national standardising body wishing to participate in the work of the Technical Committee circulate a similar statement regarding the procedure of standardisation in its own country. The letter stated that it was understood that the procedure to be followed in carrying out an international project of the type proposed would consist, first, in the submission through the respective national standardising bodies of any formal proposal that any national group might wish to make, but that thereafter correspondence on technical questions would be exchanged directly between the individual members of the Technical Committee.

The letter further stated that it was understood by the A.S.A. that Austria, France, Germany, Japan, Holland, Hungary, Switzerland and the U.S.S.R. had already expressed willingness to participate in the work of the Technical Committee; informal invitations were sent to Great Britain, Canada and Austria, which were not formally affiliated with the I.S.A., and each national standardising body intending to take part in the work was requested to designate its representative.

In the adoption at the Paris meeting of 1930 of the proposal for the creation of a Technical Committee on Nomenclature and methods of test of Petroleum Products, the General Secretary of the I.S.A. was requested to get in touch, for the purposes of co-operation, with international organisations that had already taken up the subject, such as the International Union of Pure and Applied Chemistry, the New International Association for Testing

Materials (N.I.A.T.M.), the International Electrotechnical Commission (with respect to transformer oils), etc. Whatever may have been done with this request, it is apparent that other international organisations continued previous activities or organised new activities parallel to those of Technical Committee No. 28 of the I.S.A.

An "International Petroleum Commission" was created, it is understood, as an outcome of the Third International Petroleum Conference of 1907. It was inactive during the War and for several years thereafter, but at a Conference in Zurich, either in 1929 or 1930, it was decided to extend the scope of the Commission to cover all of the technical and economic problems relating to petroleum products. In reaching such decision it appears to have been explicitly stated that there was no intention of trespassing on the field of any other existing organisation, but only of co-operating for the purposes of simplification and of avoiding duplication of work. According to the *Petroleum Zeitschrift* (January 20, 1932) the Conference adopted the following resolution :—

> "The meeting welcomes Professor Dr. Fachini's proposal to arrange for international co-operation in the mineral oil field in order to reduce the number of meetings and sessions—which take up much valuable time—in the above and allied trades and to avoid duplication of work.
>
> "For this purpose the International Petroleum Commission, the International Society of Drilling Engineers, and the members of the Mineral Oil Section of the New International Association for Testing Materials, represented at the meeting, have been invited to unite in a single organisation affiliated with the New International Association for Testing Materials with the object of promoting co-operation between manufacturers, consumers and scientists. Likewise, in the various countries, all other international and national institutes and societies of a scientific, technical and economic nature, as well as the interested authorities, should be invited to join in their respective capacities. A Sub-Committee is taking further preparatory steps, and is at the same time examining the question as to whether still further fields of operation should be included."

It is understood that this resolution had the support of the organisations named therein, of the Italian State Experimental Station for Oil Study, of the Austrian Bureau of Standards, and of the German Association for Testing Materials. One of the primary objects of the new group, designated as the "International Society for the Study of Mineral Oils," is stated to be the unification of the basic methods of testing.

If the purpose of the new organisation—or group—is as stated above, it is abundantly clear that, notwithstanding the expressed intention of the new organisation to avoid duplication and of the I.S.A. to promote co-operation, the activities of the two in this matter of testing of mineral oils will duplicate each other in their entirety, and will make the reaching of an international agreement much more difficult than if only one international organisation was involved.

In addition to this duplication of activity between the I.S.A., on the one hand, and the N.I.A.T.M. and its associates on the other, we find that in September, 1931, the International Union of Pure and Applied Chemistry, which was created in 1919 under the auspices of the International Research Council for the purpose of organising permanent co-operation between the chemical societies of adhering countries, initiated a discussion of international unification of methods of analysis of mineral oils as a preliminary to a conference in Madrid originally scheduled by the Union for April, 1932, but subsequently cancelled. The *Petroleum Times*, of London, in an editorial in its issue of January 2, 1932, states that at a meeting in Paris, October, 1931, of the Société de Chimie Industrielle, it was agreed that a standing committee should be formed to consider the practicability of arriving at international standards and methods of oil testing. Finally, mention may also be made of the International Conference on Lubricants held in Strasbourg in July, 1931.

In relation to this whole situation the A.S.A., in a letter of March 8, 1932, addressed to the several national standardising bodies, said :—

> "The objective which all have in mind is the promotion of more unified thought regarding methods of testing and nomenclature of petroleum products, and the particular machinery used to bring this about is of secondary importance. Manifestly, a necessary first step in bringing about international unification is to have the work co-ordinated on a national basis in each of the several countries that are interested in the project. In so far as co-ordination has not been accomplished, it is believed that the national standardising bodies are in a position to effect this desirable arrangement. Discussions regarding international unification could then be carried on by the several national standardising bodies through the established channels of the I.S.A. with the co-operation of existing international organisations as decided upon at the I.S.A. Conference held in Paris in May, 1930. This procedure should lead to the avoidance of the duplication that will almost certainly result if efforts of groups are exerted independently through their memberships

in international organisations not primarily concerned with standardisation, nor responsible to the several national standardising bodies.

"The situation has been carefully considered by interested groups in the United States. The American viewpoint is explicitly set forth by the American Society for Testing Materials —sponsor for Sectional Committee Z. II. on Methods of Testing Petroleum Products and Lubricants, the representative of American interests in this field. A statement of the position of the A.S.T.M., approved by its Executive Committee, reads in part as follows :—

'The A.S.T.M. believes that the establishment of the International Standards Association, bringing together the national standardising bodies of a large majority of the countries of the world, provides the most effective means yet proposed of facilitating international consideration of standards. Acting in effect as a federation of the national standardising bodies, it provides a logical means of considering and comparing the various *national* standards that in one way or another clear through the national standardising body.

'We have established in this country a workable plan of formulating and approving American standard methods of test and nomenclature for petroleum products. The A.S.T.M. is sponsoring this work through the Sectional Committee procedure and many methods of test have been approved, either as American Standard or Tentative American Standard by the A.S.A. It is, therefore, not only logical, but we believe effective, that for international consideration of these methods we should work directly through the A.S.A. with other national standardising bodies through the medium of the I.S.A.'

"We are bringing this to your attention in order that you may inform interested groups in your several countries of the American attitude.

"We hope that the groups concerned with this project in each country will decide to concentrate their efforts through their national standardising body—in so far as they have not already done so. This viewpoint is based on the belief that co-operation between all international organisations in this field is highly desirable, and that the unification of efforts within the various countries should be taken care of by the respective national standardising bodies and should centre internationally in the I.S.A."

The American Committee of the World Power Conference supports the position taken by the A.S.A. as the only apparently practical

means for securing effective action within any reasonable time on nomenclature and methods of test of petroleum products.

With respect to international standardisation in general, the American Committee is primarily concerned, as it assumes the World Power Conference is, in having such activities effectively organised nationally and internationally with the minimum of cost and without duplication. There may have appeared to be justification, originally, for creating several different international standardisation associations, and it might be possible to so draw the lines between existing organisations that their several fields would be clearly delimited; but it is notorious that such organisations once created are very prone to encroach on each other's territory, and it is certain that the cost and the difficulty of reaching results is thereby multiplied. The power and fuel interests represented in the World Power Conference have a practical stake in this matter, for standardisation affects all their equipment and products. It is time that some organisation of world-wide scope, like the World Power Conference, having a direct interest in standardisation matters but having no intention on its own part of engaging in any standardisation activity, should protest at the continually increasing difficulty and cost of reaching international agreements because of the number of organisations involved, the overlapping of their activities and the rivalries between them. Unless the situation is taken in hand before important projects have been started and permanent committees created in these several organisations, it will be difficult, if not impossible, to prevent continuous duplication. Effective unification of activities must start from the different countries. If each of these will consolidate its own standardisation activities, it will then be far easier to agree on the international organisation through which the national groups shall work, or to force real and effective co-operation if more than one international organisation is to be employed.

It is recommended that the World Power Conference disclaim any intention whatever of engaging in standardising activities itself; and, having done so, that it assert as an organisation representing the power industry of the world its direct interest in the results of standardisation and in the means by which they are to be brought about, that it recommend to its National Committees that they seek to secure unification of standardising agencies in their own countries, and that it give its support to any movement looking either toward actual and effective co-operation between existing international standardising agencies or toward their consolidation.

Note by Honorary Editor.

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The World Power Conference International Executive recently appointed the following Committee to report and to explain the possibilities of eliminating the overlapping that now exists :—

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Informal meetings have been held and very definite progress has been made.

REVIEWS.

TECHNICAL DATA ON FUEL. Third Edition. Edited by H. M. Spiers. Pp. xv.+302. London : The British National Committee, World Power Conference. 12s. 6d.

The third edition of this valuable collection of technical data is very welcome. It is indicative of the book's value that a third edition should already have been called for, and it is clear that if it continues to expand at the present rate it will become an outstanding work of reference. It is indeed likely to outgrow its name, and a title suggestive of the wide scope of the Power Conference itself might prove more suitable.

A further 60 pages have been added since the last edition, and all the new tables and descriptive matter maintain the high authoritative standard of the past. With the rapid development of the Refrigeration Industry in this country the new section on the Thermodynamic Properties of Materials should prove very useful, though it is just a slight pity that the data, taken from various sources, are not all expressed in the same manner. New aspects of heat transference, too, are taken care of in this section by introduction of tables on the Properties of Saturated Vapour of Mercury and Diphenyl Oxide.

It is pleasing to note that even the older subject-matter is being continually revised. The section on Fluid Flow in Pipes has been brought up to date by the incorporation of recent data, but it is to be regretted that the nomogram, Fig. 10, is not only indistinct but requires explanation owing to its having been disassociated from Fig. 9, of which it is an integral part.

The Editor and The British National Committee are to be congratulated on the high standard of the compilation, which will prove as useful in the works as in the testing room or laboratory. S. J. M. AULD.

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